Development of novel methodologies and fundamental studies on the compositional separation of polyethylene by High temperature liquid adsorption chromatography

Vom Fachbereich Chemie
der Technischen Universität Darmstadt
zur
Erlangung des akademischen Grades eines

Doktor-Ingenieurs (Dr.–Ing.)

genehmigte
Dissertation

vorgelegt von

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Tag der Einreichung: **20.10.2014**
Tag der mündlichen Prüfung: **08.12.2014**

Darmstadt 2014

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To my Mom, Dad, Brother and Sister
For all the support and encouragement

Acknowledgements

It is a pleasure to thank all the people who have accompanied and supported me throughout this scientific work. I am honoured to pay my sincere thanks to my research supervisor Prof. Dr. Matthias Rehahn for giving me the opportunity to work in his fascinating research group.

I wish to extend my deepest appreciation to Dr. Robert Brüll, Dr. Tibor Macko, Dr. Rongjuan Cong and Dr. Willem deGroot for providing this very interesting and challenging topic. I would like to express my gratitude to the above and to Dr. Zhe Zhou, Dr. Frank Malz, Mr. A. Parrott, Dr. W. Yau and Dr. D. Gillespie for always providing me with excellent guidance which was instrumental to the success of this research.

I would also like to thank Dr. M. Cheatham, Dr. P. Arnoudse, Dr. W. Winniford, Dr. J. Lyons, Dr. M. Miller, Dr. D. Lee, Dr. A. Pastzor Jr. from The Dow Chemical Co. for their invaluable inputs during the course of my PhD.

I want to express my gratitude for my colleagues from Fraunhofer LBF (and erstwhile DKI) for the pleasant working atmosphere and the cooperativeness in everyday matters. It was nice to meet you all and thank you very much for the beautiful moments that we spent together.

I gratefully acknowledge The Dow chemical Company for funding this PhD, as well as for the several enjoyable tour invitations and excellent care. I am also thankful in particular for the necessary freedom that I had in dealing with the direction of the present research work.

Most importantly, I am ever so grateful to my dearest Mom, Dad, Brother and Sister-in-law for their moral support, endless love, trust, and understanding during my study. Their motivational nature and enthusiasm in both good and difficult times will remain in my memory. Without them this would not be possible.

Diese Arbeit wurde unter der Leitung von Herrn Prof. Dr. Matthias Rehahn und Dr. Robert Brüll am Bereich Kunststoffe des Fraunhofer LBF (zuvor DKI) in der Zeit vom September 2011 bis zum Dezember 2014 durchgeführt.

This study is a result of the work carried out from September 2011 to December 2014 at Plastic Division, Fraunhofer LBF (previously DKI) under the supervision of Prof. Dr. Matthias Rehahn and Dr. Robert Brüll

Publication List

Journal articles

1. "One-Step Method for Separation and Identification of n‑Alkanes/ Oligomers in HDPE Using High-Temperature High-Performance Liquid Chromatography"
   D. Mekap, T. Macko, R. Brüll, R. Cong, A. W. deGroot, A. Parrott, W. Yau
   Macromolecules, 2013**,** 46, 6257-6262

2. "Liquid chromatography at critical conditions of polyethylene"
   D. Mekap, T. Macko, R. Brüll, R. Cong, A. W. deGroot, A. Parrott, P.J.C.H. Cools, W. Yau
   Polymer, 2013, 54, 5518-5524

3. "Multiple-Injection Method in High Temperature Two - Dimensional Liquid Chromatography (2D HT-LC)"
   D. Mekap, T. Macko, R. Brüll, R. Cong, A. W. deGroot, A. Parrott, W. Yau
   Macromol. Chem. Phys., 2014, 215, 314-319

4. "Studying binary solvent mixtures as mobile phase for Temperature Gradient Interactive Chromatography (TGIC) of poly (ethylene-*stat*-1-octene)"
   D. Mekap, T. Macko, R. Brüll, R. Cong, A. W. deGroot, A. Parrott
   Ind. Eng. Chem. Res., 2014, 53, 151

5. "Interactions of polyethylene with graphite in the presence of solvent by High Temperature Thermal Gradient Interactive Chromatography, Thermal Gradient NMR and solution Differential Scanning Calorimetry"
   D. Mekap, F. Malz, R. Brüll, Z. Zhou, R. Cong, A. W. deGroot, A. Parrott
   Macromolecules, 2014 (peer review)

6. "Application of alternative solvents as mobile phase for Crystallization Elution Fractionation (CEF)"
   D. Mekap, T. Macko, R. Brüll, R. Cong, A. W. deGroot, A. Parrott, 2014 (in preparation)

7. "Influence of type comonomer branch on the compositional separation of poly (ethylene-*stat*-1-alkenes) by Temperature Gradient Interaction Chromatography (TGIC)"
   D. Mekap, T. Macko, R. Brüll, R. Cong, A. W. deGroot, A. Parrott, 2014 (in preparation)

Oral presentations

1. "High temperature Liquid Chromatography (HT-LC) – Making this new technique fit for industrial application"
   4th International Conference on Polyolefin Characterization (ICPC), Houston, USA, 22 Sept. 2012.

2. "Novel method for separation and identification of n-alkanes/oligomers in HDPE by High Temperature High Performance Liquid Chromatography"
   Society of Plastic Engineers (SPE) - Polyolefin Conference, Houston, USA, 25 Feb. 2014.

Conference posters

1. "High temperature Liquid Chromatography (HT-LC) – Making this new technique fit for industrial application"
   4th International Conference on Polyolefin Characterization (ICPC), Houston, U. S. A, 22 Sept. 2012.

2. "Liquid Chromatography at Critical Condition (LCCC) of Polyethylene"
   5th International Conference on Polyolefin Characterization (ICPC), Valencia, Spain, 23 Sept. 2014.

3. "Novel method for separation and identification of n-alkanes/oligomers in HDPE by High Temperature High Performance Liquid Chromatography"
   5th International Conference on Polyolefin Characterization (ICPC), Valencia, Spain, 23 Sept. 2014.

4. "Determination of critical conditions (LCCC) for Polyethylene with three different methods"
   20th International Symposium on Separation Science, Prague, Czech Republic, Sept. 2014.

"… from so simple a beginning endless forms most beautiful and most wonderful have been, and are being, evolved."

Charles Darwin (1809-1892)

Contents

1. Summary in German

Polyolefine sind, gemessen am Volumen, die wichtigsten synthetischen Polymere mit einer für das Jahr 2020 prognostizierten jährlichen Produktion von 200 Mio. Tonnen. Auf Grund ihres in hohem Maße anpassbaren Eigenschaftsprofils, gepaart mit einem guten Kosten-Nutzen-Verhältnis, finden sie kontinuierlich Aufnahme in neuen Anwendungen. Diese Vielseitigkeit basiert auf der Fähigkeit, als Ergebnis von Fortschritten bei der Katalysator- und Herstellungstechnologie, molekulare Heterogenitäten kontrollieren zu können. Damit geht die Notwendigkeit einher, passende und umfassendere analytische Methoden für die molekulare Charakterisierung zu entwickeln. Die molekularen Heterogenitäten in Polyolefinen können im Wesentlichen durch die Molekulargewichtsverteilung (*molecular weight distribution*, MWD) und die Verteilung hinsichtlich der chemischen Zusammensetzung (*chemical composition distribution*, CCD) definiert werden. In jüngster Vergangenheit hat sich die Hochtemperatur-Hochleistungsflüssigkeitschromatographie (*high temperature high performance liquid chromatography* HT-HPLC) in Form der Hochtemperatur-Wechselwirkungschromatographie (*high temperature liquid adsorption chromatography*, HT-LAC) zu einer Methode mit zunehmender Bedeutung für die Bestimmung der CCD von Polyolefinen entwickelt. Ziel der vorliegenden Dissertation ist es, basierend auf der HT-LAC verbesserte Methoden für die Trennung von Polyethylen (PE) nach dessen Zusammensetzung zu entwickeln und die der Trennung zu Grunde liegenden Mechanismen zu untersuchen. Die Entwicklung der HT-LAC zu einer Methode zur Bestimmung der CCD von Polyolefinen ist das Ergebnis der Entdeckung, dass poröser Graphit (*porous graphitic carbon*, PGC) Polyolefine und Olefincopolymere reversibel aus einer Lösung adsorbieren und daher als stationäre Phase eingesetzt werden kann. Die Forschung, die in dieser Dissertation präsentiert wird ist in fünf Abschnitte gegliedert, die jeweils zu Publikationen geführt haben und die in kumulativer Form die unten angegebenen Hauptschlussfolgerungen umfassen. Im Anschluss an eine Zusammenfassung des Stands der Technik werden die Schlussfolgerungen für jeden Teil individuell zusammengefasst.

Abhängig vom Trennmechanismus können HT-HPLC Techniken in Hochtemperatur-Größenausschlusschromatographie (*high temperature size exclusion chromatography*, HT-SEC) und HT-LAC unterteilt werden. HT-SEC wird routinemäßig angewendet, um die MWD von Polyolefinen zu bestimmen, wohingegen HT-LAC erst kürzlich entwickelt wurde, um die

CCD derselben zu bestimmen. Entsprechend des Parameters, welcher die Trennung steuert kann HT-HPLC weiter in Lösungsmittelgradienten-Wechselwirkungschromatographie (*high temperature solvent gradient interaction chromatography*, HT-SGIC) und Wechselwirkungschromatographie mit Thermischen Gradienten (*high temperature thermal gradient interaction chromatography*, HT-TGIC) unterteilt werden. Bei der HT-SGIC wird der Analyt durch die Anwendung eines Gradienten von einem adsorptionsfördernden Lösungsmittel zu einem desorptionsfördernden bei isothermen Bedingungen getrennt, wohingegen dies bei der HT-TGIC durch die Anwendung eines Temperaturgradienten mit einer isokratischen mobilen Phase erreicht wird. An der Grenze zwischen HT-SEC und HT-LAC existiert ein dritter chromatographischer Modus, genannt Hochtemperatur-Flüssigkeitschromatographie bei kritischen Bedingungen (*high temperature liquid chromatography at critical conditions*, HT-LCCC), der als Teil dieser Dissertation zum ersten Mal beschrieben wird. Die Wechselbeziehung zwischen der Verteilung im Hinblick auf die Zusammensetzung und derjenigen hinsichtlich des Molekulargewichts kann durch Koppeln der entsprechenden Trennungen in einem Kreuzfraktionierungsansatz untersucht werden. Technisch wurde dies in Form von zweidimensionaler HT-LC (*two dimensional HT-LC*, 2D HT-LC) realisiert, welche die HT-LAC und HT-SEC zusammenführt, um die bivariate CCD x MWD zu entschlüsseln.

Im ersten Teil wurde unter Verwendung von HT-SGIC eine neuartige Ein-Schritt-Methode entwickelt, um n-Alkane/Oligomere in PE zu trennen und zu identifizieren. n-Alkane sind als Nebenprodukt der katalytischen Synthese ein Bestandteil von PE, und sie stellen den Hauptbestandteil von Wachsen, Ölen und Schmierstoffen dar. Daher ist eine akkurate Trennung und Identifizierung von Alkanen für die Industrie entlang der gesamten Wertschöpfungskette von Polyolefinen von großer Bedeutung. Im Allgemeinen wird bei einem HT-SGIC-Experiment die Probe zuerst aus einem adsorptionsfördernden Lösungsmittel auf der Oberfläche von PGC adsorbiert und dann durch Anwendung eines Lösungsmittelgradienten zu einem desorptionsfördernden Lösungsmittel selektiv desorbiert. Durch Verlängerung der Dauer des Gradienten, Reduktion der Unterschiede bezüglich der Lösungsmittelqualität zwischen dem adsorptionsfördernden und dem desorptionsfördernden Lösungsmittel und durch Reduzieren der Temperatur wurde es möglich lineares PE mit durchschnittlichen Molekulargewichten im Bereich von 0,74 – 2 kg/mol in die einzelnen Alkane zu trennen. Letztere wurden durch Versetzen der Analyten mit Alkanen bekannten

Molekulargewichts und durch Verwendung Matrix-unterstützter Laser-Desorptions/Ionisations-Massenspektrometrie als komplementärer Technik bestimmt. Auf diese Weise konnten n-Alkane mit Kohlenstoffzahlen zwischen 18 und 180 getrennt und identifiziert werden. Diese Methode wurde des Weiteren verwendet, um als Beweis der Anwendbarkeit n-Alkane in einem industriellen PE hoher Dichte (*high density PE*, HDPE) zu detektieren. Die entwickelte Methode liefert einen schnellen Ein-Schritt-Prozess, um n-Alkane/Oligomere in PE ohne vorherige Aufbereitung, etwa in Form von Extraktion und Aufkonzentrieren, zu trennen und nachzuweisen.

Bei der Kopplung zweier analytischer HT-HPLC Techniken (zum Beispiel 2D HT-LC, HT-LAC x HT-SEC) findet eine signifikante Verdünnung des Analyten statt, wenn die Fraktionen aus der ersten Dimension in die zweite Dimension übertragen werden. Folglich verringert sich die Intensität des detektierten Signals, was zu geringen Signal-zu-Rausch-Verhältnissen führt. Ein Schlüsselschritt für die 2D HT-LC zu einer Routinemethode ist es daher, die Signalintensität zu erhöhen. Als Teil der durchgeführten Experimente wurde beobachtet, dass eine PE-Probe mehrmals injiziert und auf der PGC-basierten stationären Phase der ersten chromatographischen Dimension (HT-SGIC) adsorbiert werden konnte ohne den Lösungsmittelgradienten zu starten. Die akkumulierte adsorbierte Probe kann dann in einem einzigen Schritt mit der Hilfe eines Lösungsmittelgradienten desorbiert werden. Dieser Ansatz wurde erfolgreich verwendet, um die detektierten Signale signifikant zu erhöhen und in eine Verbesserung des Signal-zu-Rausch-Verhältnis der 2D HT-LC Trennung umgesetzt.

Die Trennung bei der HT-SEC wird durch Änderungen der konformativen Entropie der polyolefinischen Makromoleküle in der mobilen Phase bestimmt, wenn sie in die Poren der stationären Phase eindringen, während bei der HT-SGIC die Trennung durch die enthalpischen Wechselwirkungen zwischen den Makromolekülen und der stationären Phase in der Anwesenheit einer mobilen Phase bestimmt wird. HT-LCCC ist ein wichtiger chromatographischer Modus an der Grenze zwischen HT-SEC und HT-SGIC, wo die enthalpischen Wechselwirkungen den entropischen Term ausgleichen. Infolgedessen eluieren die Makromoleküle einer Wiederholungseinheit unter diesen Bedingungen unabhängig vom Molekulargewicht. Bedingungen für LCCC sind für eine Vielzahl von bei Raumtemperatur löslichen Polymeren bekannt. Die Kenntnis von Bedingungen für HT-SEC und HT-SGIC, d.h. geeigneter stationärer und mobiler Phasen, ist eine Voraussetzung um HT-LCCC zu

realisieren. Nach der Erarbeitung von Bedingungen für die HT-SGIC ist es daher eine interessante Frage, ob solche Bedingungen für PE identifiziert werden können. Unter Verwendung wohl definierter linearer PE-Standards variierender und bekannter durchschnittlicher Molekulargewichte und durch iterative Kombination adsorptions- und desorptionsfördernder Lösungsmittel wurden Bedingungen für die HT-LCCC von PE etabliert. Die festgelegten Bedingungen für HT-LCCC wurden durch zwei gut bekannte empirische Methoden verifiziert. Um die Anwendbarkeit von HT-LCCC auf die Trennung von Poly(ethylen-*stat*-1-octen)(E/O) Proben mit vergleichbarem Molekulargewicht nach Zusammensetzung zu demonstrieren, wurden diese nach ihrem durchschnittlichen 1-Octen-Gehalt getrennt.

Der vierte Teil war auf die Verbesserung der Auflösung der Trennung bei der HT-TGIC von E/O-Copolymeren fokussiert. Bisher sind 1,2-Dichlorbenzol (ODCB) und 1,2,4-Trichlorbenzol (TCB) die mobilen Phasen der Wahl für HT-TGIC. Die im vorherigen Abschnitt durchgeführte Entwicklung von HT-LCCC führte zu einem besseren Verständnis des Effekts, den ein binäres Lösungsmittelsystem auf das chromatographische Elutionsverhalten hat. Dies warf die Frage auf, ob binäre mobile Phasen eingesetzt werden könnten, um die Auflösung bei der HT-TGIC zu verbessern. Dies wurde am Beispiel von E/O-Copolymeren unter Verwendung von Lösungsmitteln, die sich in ihrer Lösungsqualität und ihrem adsorptionsfördernden Verhalten unterscheiden, sondiert. Die Lösungsmittel, die Teil dieser Studie waren, waren 1-Decanol, n-Decan, ODCB, TCB und Diphenylether. Durch Vergleich der Ergebnisse der oben genannten Experimente und mit Hilfe theoretischer Berechnungen wurde ermittelt, dass 40/60 (v/v) n-Decan/TCB und 30/70 (v/v) 1-Decanol/TCB die höchste chromatographische Auflösung bei der Trennung von E/O-Copolymeren mittels HT-TGIC ermöglichen. Diese optimierten Systeme wurden auch angewendet, um als Proof of Concept einen Modellblend zu trennen.

Die oben genannten Studien über HT-TGIC konzentrierten sich auf die Kontrolle der Trennung der olefinischen Makromoleküle unter Verwendung von PGC als stationärer Phase und eines Temperaturgradienten in einer isokratischen mobilen Phase. Eine wichtige Frage ist daher die nach der Natur der Wechselwirkungen zwischen den Makromolekülen und der graphitischen Oberfläche. Für n-Alkane und weitere Analyten niedrigen Molekulargewichts

wurde nachgewiesen, dass diese Wechselwirkungen auf Van-der-Waals- und London-Kräften basieren.

Jedoch liegt der Fall für PE auf Grund der Komplexität, die aus den verschiedenen molekularen Heterogenitäten erwächst, anders. Zusätzlich ist PE teilkristalliner Natur und Kristallisation könnte auch eine Rolle spielen. Daher wurde Kernspinresonanzspektroskopie (*nuclear magnetic resonance*, NMR) unter Variation der Temperatur als NMR mit thermischen Gradienten (*thermal gradient NMR*, TG-NMR) durchgeführt, um die Wechselwirkungen im System PE/Graphit/ODCB zu untersuchen und den Mechanismus HT-TGIC basierter Trennungen zu verstehen. Eine Herausforderung, die dabei überwunden werden musste, war die Tatsache, dass PGC, welches gemeinhin als stationäre Phase in der HT-LAC benutzt wird, sich im NMR-Röhrchen auf Grund seiner im Vergleich zu ODCB höheren Dichte absetzte. Dieses Problem wurde gelöst, indem Nanographit (NG), dessen Dichte mit der von ODCB vergleichbar ist, verwendet wurde. Die experimentellen Bedingungen wurden zum einen weiter optimiert, um das Absetzen von NG zu verhindern, und zum anderen, um ein gutes Signal-zu-Rausch-Verhältnis für das gelöste PE zu erreichen. Mittels der TG-NMR-Experimente wurde herausgefunden, dass die Konzentration von PE Homopolymeren in der Lösung sich ca. 50 °C oberhalb der Kristallisationstemperatur aus der Lösung zu verringern beginnt. Durch wiederholte Messungen für jeden Temperaturschritt konnte bestätigt werden, dass diese Verringerung nicht auf einen Nicht-Gleichgewichts-Zustand zurückzuführen ist. Die Verringerung der Konzentration ist vollständig und ohne Hysterese bei Erhöhung der Temperatur reversibel. Eine analoge Verringerung der Konzentration in Lösung wurde auch für ein vollständig amorphes E/O-Copolymer gefunden. Das Fehlen einer Hysterese und die Tatsache, dass auch die Konzentration eines amorphen Copolymeren in Lösung nach Abkühlung vermindert ist, deuteten darauf hin, dass die Wechselwirkungen zwischen dem Graphit und dem Polymer adsorptiver Natur sind und induzierte Kristallisation keine oder eine untergeordnete Rolle spielt. Um dies weiter zu überprüfen wurden für beide Proben Lösungs-Kalorimetrie-Experimente unter Verwendung von NG und ODCB durchgeführt. Anhand des Wärmeflusses in der Kühlphase konnte kein thermischer Übergang ermittelt werden, der auf eine induzierte Kristallisation hindeutet. In summa kann somit über diesen indirekten Beweis eine Adsorption der Makromoleküle als Mechanismus der Trennung in der HT-TGIC bestätigt werden.

Diese Arbeit unterstützt das Verständnis der Trennung nach Zusammensetzung von Polyolefinen mit der Hilfe von HT-HPLC und eröffnet neue Möglichkeiten für die Trennung von komplexeren polyolefinischen Makromolekülen nach Zusammensetzung in der Zukunft. Die Methodenentwicklung zur Trennung von Oligomeren erweitert den Anwendungsbereich der HT-SGIC auf die Trennung und Identifizierung von linearen Oligomeren. Hieraus ergeben sich beispielsweise Perspektiven für die Trennung von verzweigten Oligomeren. Die entwickelte Mehrfachinjektionstechnik ist ein Schlüsselschritt für 2D HT-LC Trennungen im Hinblick auf die Anwendung als quantitative Methode und zum Nachweis von Minderheitskomponenten. Die neu entwickelten HT-LCCC Trennungen des PE können auf andere olefinische Homo- und Copolymere erweitert werden, um zukünftig dem analytischen Bedarf des sich rasch entwickelnden Gebietes der segmentierten Olefincopolymere Rechnung zu tragen. Die Anwendung von gemischten mobilen Phasen bei der HT-TGIC verbesserte die Auflösung der Trennung von E/O-Copolymeren und kann darüber hinaus auf andere Lösungsmittel- und Polymersysteme erweitert werden. Die Auseinandersetzung mit der TG-NMR erweiterte das Verständnis der Wechselwirkungen in PE/Graphit/Lösungsmittel-Systemen bei variablen Temperaturen. Dieses Wissen kann zu einer besseren Kontrolle über Trennungen mittels HT-TGIC genutzt werden. Perspektivisch stellt die TG-NMR-Methode ein leistungsfähiges Verfahren für das Screening von möglicherweise für die Wechselwirkungschromatographie einsetzbaren stationären Phasen im Hinblick auf ihre Selektivität dar.

2. Introduction and Preface

Polyolefins are, by volume, the most important commodity polymers with an annual production expected to reach 200 million metric tons by the year 2020. Due to their versatile application properties paired with an excellent cost/performance ratio, polyolefins continue to find acceptance in many novel and diverse applications. This versatility arises from the ability to control the molecular heterogeneities, microstructure and architecture of the macromolecules through advances in catalyst and process technology. At the same time, this infers the need to develop appropriate analytical methodologies for molecular characterization. The molecular heterogeneities in polyolefins are primarily defined by their distribution with regard to molecular weight and chemical composition.

High temperature liquid adsorption chromatography, HT-LAC, has emerged as a new technique for the compositional separation of polyolefins in 2009 and is currently experiencing great attention in academia and industry as an alternative to traditional methods used for this purpose which relied on crystallization. The aim of the work presented in this thesis was to develop improved HT-LAC methodologies, and investigate the underlying fundamentals behind the compositional separation of polyethylene by HT-LAC. This research was funded by the *Dow Chemical Company* and formed part of a joint collaboration between the Material Analytics Group from *Fraunhofer LBF* and the Performance Plastics Characterization and Testing Group from the *Dow Chemical Company.*

This thesis may be divided into three parts. The first one comprising chapter 4 and 5 provides a general overview of polyolefins as material and the state of the art in characterization techniques, which are applied to study the different molecular heterogeneities present in polyolefins. The second part formed by chapter 6 showcases the research work conducted as five publications in cumulative form. And finally, chapter 7 summarizes the conclusions from the research conducted as part of this thesis.

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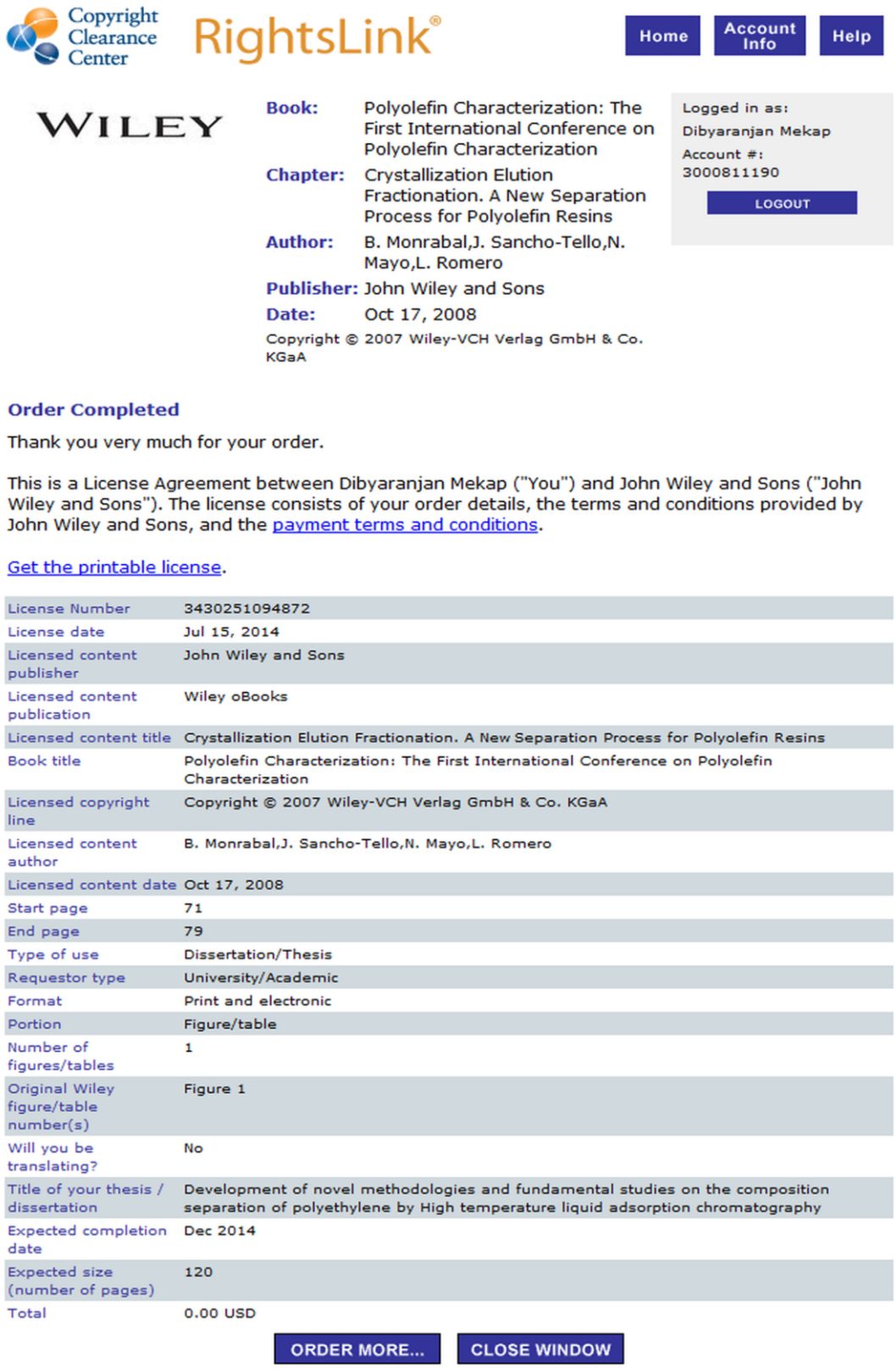
Figure 5: Separation diagram by crystallizability for a) TREF and b) CEF. Note: T_i and T_f are initial and final temperatures in the column.



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Book: Polyolefin Characterization: The First International Conference on Polyolefin Characterization
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Figure 6: Contour plot obtained by 2D HT-LC of a blend of HDPE, PP of varying tacticity and ethylene/propylene copolymers.

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Figure 7: Cooling curves in the crystallization range of LDPE. Sample mass 4 mg in 25 mg aluminium pan for cooling rate up to -20 °C/min and of 0.4 mg in 2 mg aluminium foil for higher rates. Heat capacity is plotted downwards (Perkin-Elmer Pyris 1 DSC).

Figure 8: Comparison of weight fraction versus temperature from solution DSC and CRYTSAF for same metallocene polymers.

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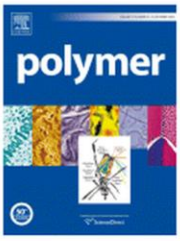

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Figure 10: ^{1}H NMR from TG-NMR of E/O copolymer in the temperature range 120 → 70 °C in 10 °C steps. Focused on chemical shift range: 5.8 – 4.6 ppm.

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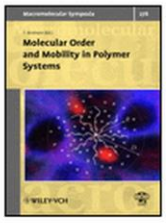

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Author: Zhe Zhou,Rongjuan Cong,Yiyong He,Manjiri Paradkar,Mehmet Demirors,Mike Cheatham,A. Willem deGroot

Publication: Macromolecular Symposia

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Author: D. Mekap, T. Macko, R. Brüll, R. Cong, A. W. deGroot, A. Parrott, and W. Yau

Publication: Macromolecules

Publisher: American Chemical Society

Date: Aug 1, 2013

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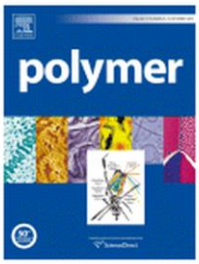

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Author: D. Mekap,T. Macko,R. Brüll,R. Cong,A.W. deGroot,A. Parrott,P.J.C.H. Cools,W. Yau

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4. Theoretical consideration - I: Introduction to polyolefins

Polyolefins belong to the class of commodity polymers and are by volume the most produced synthetic polymers worldwide with an annual production of 147 million tons in 2011 which is expected to grow up to 170 million tons by 2017[1]. Their most prominent advantages include an excellent cost/performance ratio and great versatility with regard to end-use properties. Apart from these, polyolefins also exhibit other excellent properties like high mechanical strength, chemical resistance, processability and non-toxicity which make them the material of choice for a wide range of applications. A large variety of polyolefins is available in the market today, each representing a set of properties suited to specific applications. To study them better they are classified into different groups as detailed in the subsequent sections.

4.1 Classification based on density (traditional)

According to the underlying main monomer, polyolefins can be broadly divided as polyethylene (PE), polypropylene (PP) and olefin based elastomers (e.g., ethylene/propylene/diene terpolymers, EPDM). PE is the most widely used polyolefin and will be the focus of this thesis.

PE has traditionally been classified based on a density range (Table 1) into high density PE (HDPE), low density PE (LDPE) and linear low density PE (LLDPE).

Table 1: Density ranges of different PE.

Type of PE	Density range (g/cm^3)
HDPE	0.945-0.97
LDPE	0.915-0.935
LLDPE	0.915-0.94

Any PE with a density below 0.9 g/cm^3 is referred to as ultra-low density PE (ULDPE), while for PE with a density range of 0.88 – 0.915 g/cm^3 the term very low density PE (VLDPE) is also in use. A density based classification gives no information about the molecular microstructure which is an important determinant of the end-use properties of the PE, but being a popular convention, the density based nomenclature will be also followed in the subsequent topics covered in this thesis.

4.2 Classification based on microstructure

Another criterion for classifying PE is its microstructure i.e., the way the monomers are linked in the polymer chain in terms of regio- and stereochemistry as well as their sequence. The microstructure is controlled by the mechanism of polymerization. LDPE is manufactured via a free-radical process which results in statistically branched macromolecules having both short chain (SCB) and long chain (LCB) branches. During the free radical polymerization process the propagating chain radical can undergo intramolecular backbiting resulting in SCBs, or can undergo intermolecular chain transfer to polymer chains already formed resulting in LCBs.[2] This statistical microstructure endows LDPE with its distinctive properties – clarity, flexibility, impact resistance and processability.

The majority of commercial HDPE and LLDPE is produced either with Ziegler-Natta or Philips catalysts which only result in SCBs and essentially no LCBs. Metallocene catalysts emerged in the 1980s and, due to their single site nature, allow better control over the chain microstructure. Metallocene catalysts can be applied to produce both HDPE and LLDPE. A generalized representation for the microstructure of LDPE, LLDPE and HDPE is represented in Figure 1.

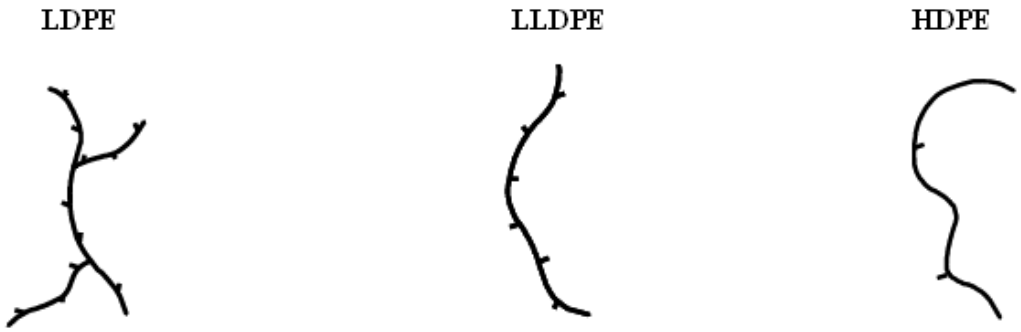

Figure 1: Classification of polyethylene according to branching structure.

Linear low density polyethylene (LLDPE) constitutes an important segment of all PE markets. LLDPEs are commonly synthesized by copolymerizing ethylene with different α-olefin comonomers like 1-butene, 1-hexene and 1-octene. LLDPE is finding many applications as its end-use properties can be conveniently tailored by varying the comonomer content and its distribution between and along the chain i.e., inter- and intramolecular heterogeneity.

4.3 Classification based on polymerization chemistry

The success story of polyolefins as a commercial polymer has been made possible by the discovery of newer and more efficient catalyst technologies. Since the 1950s when the Ziegler-Natta[3,4] and Phillips[6] catalysts were discovered, unremitting research has made these catalyst families more efficient and adaptable to process technologies. The discovery of metallocene and late transition metal based single site catalysts in the 1980s and 1990s respectively has enabled improved control over the microstructure of polyolefins. Based on history, the catalyst development for polyolefin production may be summarized as in Table 2.

Table 2: Main characteristics of coordination catalysts for olefin polymerizations. From Ref.[6]

Type of catalyst	Physical state	Examples*
Ziegler-Natta[3,4]	Heterogeneous	$TiCl_3$, $TiCl_4/MgCl_2$
	Homogenous	VCl_4, $VOCl_3$
Philips[5]	Heterogeneous	CrO_3/SiO_2
Metallocene[7,8]	Homogenous	Cp_2ZrCl_2
	Heterogeneous	Cp_2ZrCl_2/SiO_2
Late transition metal[9-11]	Homogenous	Ni, Pd, Co, Fe with diimine and other ligands

**This is not a comprehensive list. These are simply representative examples.*

Ziegler-Natta[3, 4] and Phillips[5] catalysts were the first to be used for the production of polyolefins and due to their cost advantage over organometallic single site catalysts still remain the workhorse of the polyolefin industry. The structures of Ziegler-Natta and Phillips catalysts are represented in Figure 2.

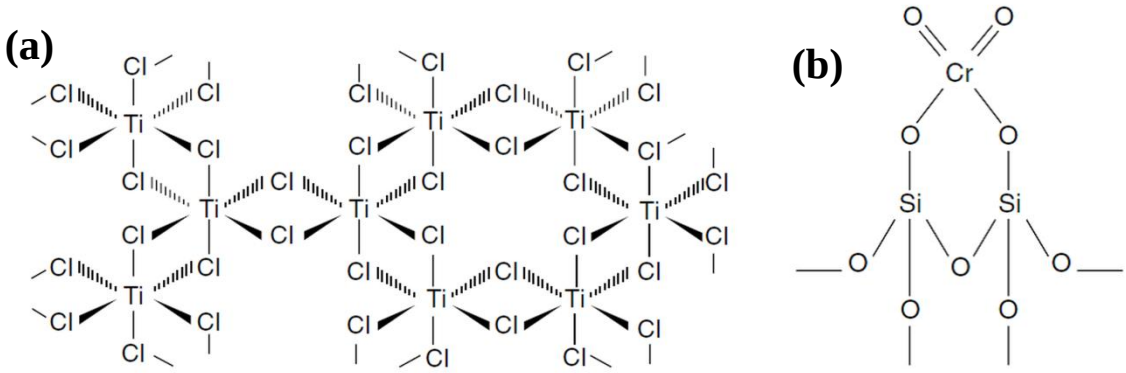

Figure 2: Structures of (a) Ziegler-Natta and (b) Philips catalysts for olefin polymerization.

These catalysts produce polyolefins with non-uniform microstructure which are characterized by broad distributions with respect to molecular weight (MWD) and chemical composition (CCD). The broader MWD and CCD of polyolefins originating from heterogeneous Ziegler-Natta and Phillips catalysts can be attributed to the presence of multiple active sites. Ziegler-Natta catalysts may also be homogenous, an example of which are the vanadium based types. These may have one reaction site and produce polyolefins with uniform microstructure.

The two remaining groups in Table 2 i.e., metallocene and late transition metals are examples of single site catalysts. The structures of these catalysts are given in Figure 3.

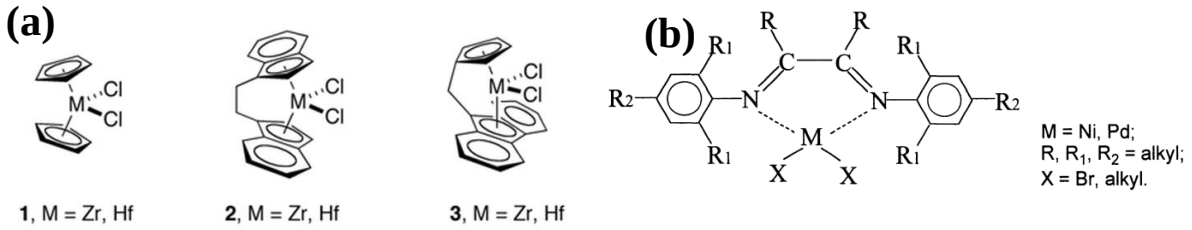

Figure 3: Structure of (a) various metallocenes and (b) late transition metal (Ni(II)/Pd(II) α-Diimine) catalysts.

Polyolefins produced via single site catalysts show uniform microstructure and narrow MWD and CCD.

Apart from these, lately there have been successes in the development of new catalysts like concurrent tandem catalysts (CTC) which have further augmented the types and applications of PE. In CTCs multiple catalysts are applied on a set of monomers in a single processing step to yield microstructures otherwise impossible to obtain with single site systems[12]. An

outcome of tandem catalysts is the development of olefin block copolymers via the chain-shuttling polymerization patented by the Dow Chemical Co.[13-15].

Catalyst technologies and polymerization processes are a prerequisite to understand the unique properties of polyolefins produced by certain catalysts. The distributions with regard to MW and CC are a direct consequence of the type of catalyst and polymerization conditions used. Hence, an accurate characterization of polyolefins in terms of MWD and CCD is of vital importance to establish structure ↔ property relationships, and in the same way to also support catalyst research.

5. Characterization of polyolefins

Polyolefins, though constituted from simple hydrocarbons, show a large variety in their molecular heterogeneities which lead to complexity in terms of characterization, but are at the same time the key for their adaptability and tailorability. The most important distributions in polyolefins are those with regard to molecular weight (MWD) and chemical composition (CCD); other molecular heterogeneities arise from unsaturation and microstructural features like inverse monomer insertion and comonomer sequence distribution. The different molecular heterogeneities in polyolefins and the common analytical techniques applied to determine these are illustrated in Figure 4.

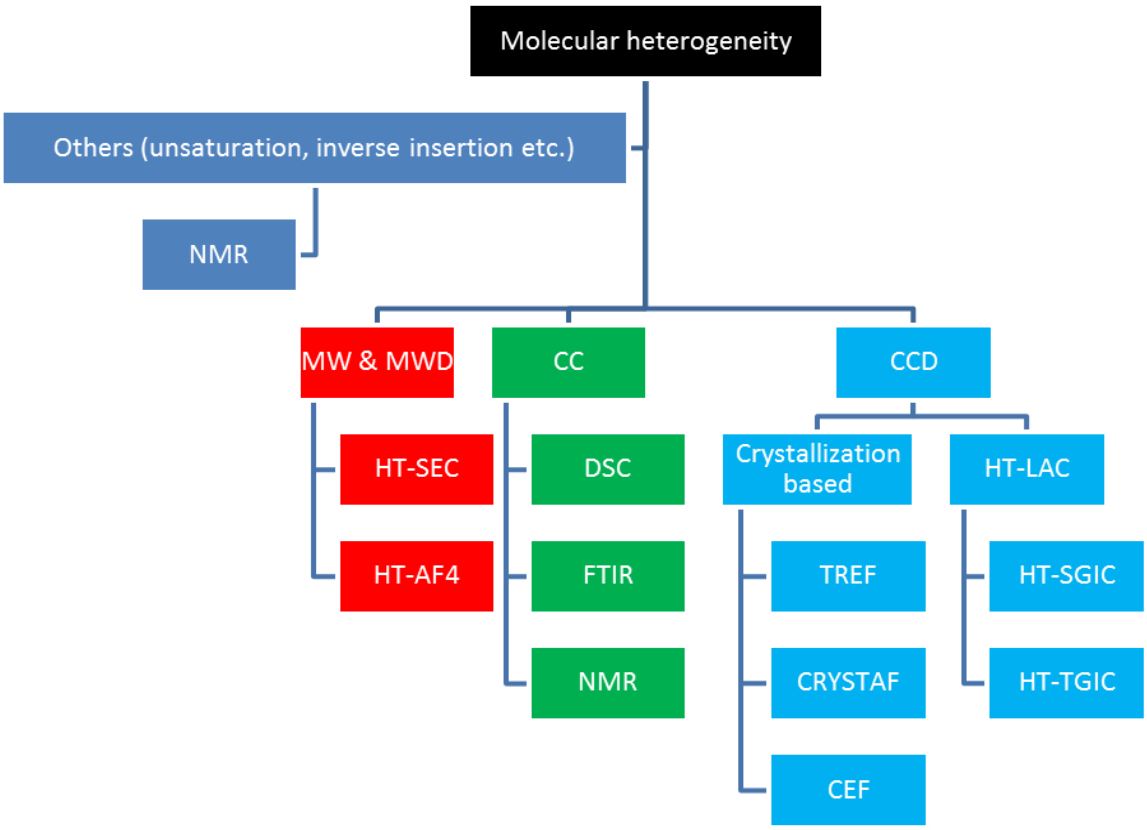

Figure 4: Molecular heterogeneities in polyolefins and analytical techniques to characterize them. Note: acronyms mentioned below.

(NMR: Nuclear magnetic resonance spectroscopy, HT-SEC: High temperature liquid adsorption chromatography, HT-AF4: High temperature asymmetric flow field flow fractionation, DSC: Differential scanning calorimetry, FTIR: Fourier transform infrared spectroscopy, TREF: Temperature rising elution fractionation, CRYSTAF: Crystallization analysis fractionation, CEF: Crystallization elution fractionation, HT-LAC: High temperature liquid adsorption chromatography, HT-SGIC: High temperature solvent gradient interaction chromatography, HT-TGIC: High temperature thermal gradient interactive chromatography)

5.1 Crystallization based techniques

For polyolefins, other than MWD, the CCD is the most important factor impacting the end-use properties, and since the 1990s crystallization based techniques have been routinely used for its determination. These techniques are based on a fractionation mechanism that relies on differences in crystallizabilities of the macromolecules from dilute solution. The crystallization of a polymer from dilute solution in general depends upon the effect that factors like solvent type, polymer molecular weight, and type and content of comonomer, have on the thermodynamic equilibrium of crystallization ↔ dissolution.

The thermodynamic equilibrium of a homopolymer solution may be described by the Flory-Huggins equation for the free energy of mixing, assuming a uniform distribution of solvent and homopolymer segments[16-20]. The depression in the equilibrium dissolution temperature of the homopolymer due to the presence of solvent and the number of chain segments is given by Eq. 1:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \left(\frac{R}{\Delta H_u}\right)\left(\frac{V_u}{V_1}\right)\left[-\frac{\ln(\nu_2)}{x} + (1-\frac{1}{x})\nu_1 - \chi_1\nu_1^2\right] \quad (1)$$

Where, T_m^0 = Melting temperature of the homopolymer,

T_m = Equilibrium dissolution temperature of the homopolymer in solution,

ΔH_u = Heat of fusion per repeating unit,

V_u and V_1 are the molar volumes of the homopolymer repeating unit and diluent, respectively,

ν_1 and ν_2 are the volume fractions of the diluent and homopolymer, respectively,

x = the number of segments, and

χ_1 = the Flory–Huggins thermodynamic interaction parameter.

However, in all crystallization based techniques the crystallization step occurs in dilute solution, and as increasing the dilution does not significantly impact the dissolution temperature[21] Eq. 1 is applicable over the entire range of concentration. Thus, for a homopolymer in a dilute solution the impact of chain length on the dissolution temperature can be quantified by rearranging Eq. 1 into Eq. 2:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{\Delta H_u}\frac{V_u}{V_1}(\nu_1 - \chi_1\nu_1^2) - \frac{R}{\Delta H_u}\left[\frac{\ln(\nu_2)}{r} + \frac{\nu_1}{r}\right] \quad (2)$$

Where, r = number of repeating units per polymer.

In Eq. 2 the second term on the right hand side which accounts for the impact of chain length shows that the equilibrium dissolution temperature drops with decreasing molecular weight[21, 22]. However, this molecular weight influence is significant only for lower values while at higher molecular weights the dissolution temperature becomes independent of the chain length and hence Eq. 2 gets simplified to Eq. 3:

$$\frac{1}{T_m} - \frac{1}{T_m^0} = \frac{R}{\Delta H_u}\frac{V_u}{V_1}(\nu_1 - \chi_1\nu_1^2) \quad (3)$$

From Eq. 3 it can be concluded that homopolymers of relatively high molecular weight crystallize at the same temperature provided their composition and other experimental parameters remains same. This fact has also been experimentally verified and the molecular weight threshold for HDPE from 1, 2-dichlorobenzene (*o*-dichlorobenzene, ODCB) stands at ~ 10,000 g/mol[23, 24].

Copolymers in dilute solution present additional complications as the dissolution temperature also depends on the interactions between the different monomeric units apart from those with the solvent molecules. Taking into account the different interactions between the comonomers and the solvent molecules, the net Flory-Huggins thermodynamic interaction parameter can be defined as in Eq. 4:

$$\chi_1 = \upsilon_A\chi_{1A} + \upsilon_B\chi_{1B} - \upsilon_A\nu_B\chi_{AB} \text{ } \textit{(For copolymer with two comonomers)} \quad (4)$$

Where, χ_1 = interaction parameter of a binary copolymer with pure solvent,

χ_{1A} and χ_{1B} are the interaction parameters of the corresponding homopolymers with the solvent,

χ_{AB} = interaction parameter between comonomers A and B in the copolymer chain,

υ_A and ν_B are volume fractions of comonomers A and B in the copolymer molecule, respectively.

For copolymers in dilute solution, the comonomer unit fraction is the most important factor that affects the crystallizability of the macromolecules. The comonomer units act as defect in the chain and interrupt its regularity, thereby lowering the crystallizability of the macromolecule. The crystallization behaviour of copolymers in dilute solution was theoretically explained by Anantawaraskul et al.[25], and experimentally proven by Alamo and Mandelkern[26] for the case of statistical copolymers of ethylene and α-olefins. The crystallization based techniques for the analysis of CCD of polyolefins may be divided according to their chronology of development into – temperature rising elution fractionation (TREF), crystallization analysis fractionation (CRYSTAF) and crystallization elution fractionation (CEF). The working principle and the advantages and disadvantages of each technique will be covered in the subsequent sections.

5.1.1 Temperature rising elution fractionation (TREF)

TREF was first reported by Desreux and Spiegels in 1950[27] and has been applied as a routine method to determine the CCD of polyolefins since the late 1980s[28, 29]. The separation in TREF is based on a two-step process of crystallization and dissolution→elution. The sample is dissolved in a thermodynamically good solvent[31] and loaded into a column packed with an inert support at elevated temperatures. The loaded column is then cooled at a constant rate with no solvent flow, whereby the macromolecules are fractionated according to differences in their crystallization temperature from the solution. In the next step the crystallized sample is re-dissolved by increasing the temperature, and eluted in a constant flow of the solvent. Analogous to variable crystallization temperatures the macromolecules re-dissolve and elute at different temperatures. These fractions can be either collected for further offline characterization (pTREF) or analyzed online with the help of a concentration-sensitive detector e.g., infra-red (IR) detector (aTREF). Crystallization is the most important step in TREF, and the cooling rate has been observed to have a strong influence on the quality of the separation with lower cooling rates resulting in a higher resolution[30]. The type of support has little to no influence on the fractionation process, and glass beads and stainless steel shots are commonly used for this purpose. The solvent of choice for TREF of polyolefins are xylene, ODCB and 1,2,4-trichlorobenzene (TCB).

Reviews on TREF have been published by Wild[29], Glöckner[31], Fonseca and Harrison[32], Soares and Hamielec[33], Anantawaraskul[25] and Monrabal[34, 35]. Soares et al. explained the broadening of the peaks in TREF observed with increasing comonomer content on the basis of Stockmayer's bivariate distribution[30]. Monrabal et al. experimentally established a linear correlation between the temperature of elution and the SCB content in TREF separations of LLDPE[33, 34]. However, TREF based separations suffer from limitations with respect to throughput and long duration of experiments, which has led to the development of other techniques as given in the next sub-sections.

5.1.2 Crystallization analysis fractionation (CRYSTAF)

CRYSTAF was developed as a faster alternative to TREF by fractionating the polyolefin sample in a single crystallization step without the elution step common to TREF[35]. Additionally, 5 samples could be analyzed simultaneously which further speeded up the characterization process. In CRYSTAF the polymer is dissolved in a thermodynamically good solvent (e.g., ODCB, TCB) at elevated temperatures inside a cylindrical reactor. Aliquots of the polymer solution are filtered out and analyzed with a concentration sensitive detector e.g., IR. The baseline is set from experimental data points taken above the crystallization temperatures. As the temperature is reduced at a fixed rate the polymer sample crystallizes out of the solution according to differences in their crystallizability or SCB/comonomer content. The portion of the sample that remains soluble even at room temperatures (30 °C) i.e., the soluble fraction (SF) represents the non-crystalline (amorphous) fraction of the sample.

Brüll et al. showed the separations by CRYSTAF to be independent of the length of comonomer unit for different propene/α-olefin[36] and ethylene/α-olefin[37] statistical copolymers, varying in the type of α-olefins (1-octene, 1-decene, 1-tetradecene, and 1-octadecene). Sarzotti et al. reported that MW influences on the crystallization temperature in CRYSTAF disappeared above the M_w value of 10,000 g/mol with the help of ethylene/1-hexene statistical copolymers[38]. Analogous to TREF, the peaks in CRYSTAF also exhibit broadening with increasing comonomer content as explained theoretically with the help of Stockmayer's distribution[39]. CRYSTAF has been applied to separate blends of HDPE/LDPE[40] and PE/PP[40-42]. CRYSTAF separations show a linear correlation between the crystallization temperature and the comonomer content of LLDPE[34, 35] similar to TREF. However, although

both TREF and CRYSTAF are based on the principle of crystallization TREF has been established to show better resolution as compared to CRYSTAF[6]. Thus, a necessity existed for a method which shows similar resolution as TREF and at the same time overcomes the bottleneck of long analysis time. This led to the development of crystallization elution fractionation (CEF) which is described next.

5.1.3 Crystallization elution fractionation (CEF)

CEF achieves resolution comparable to TREF and enables faster analysis by applying the concept of *dynamic crystallization*. The separation in TREF and CEF is shown in Figure 5 as reported by Monrabal et al.[43]

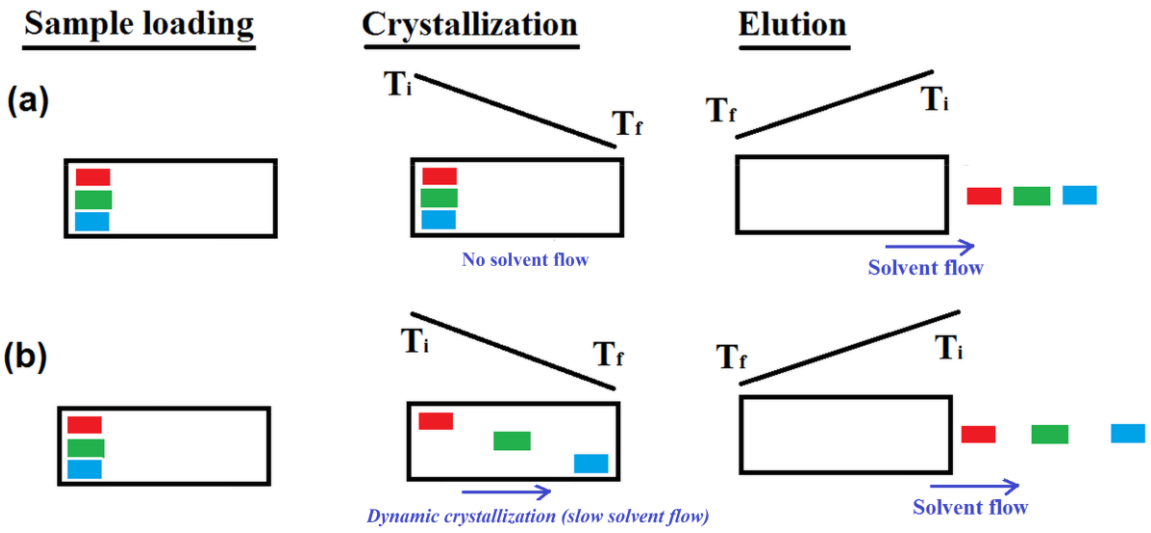

Figure 5: Separation diagram by crystallizability for a) TREF and b) CEF. Note: T_i and T_f are initial and final temperatures in the column. From Ref.[43]

In dynamic crystallization the different components of a sample are separated from each other in the crystallization step, during which a very slow flow of solvent is maintained[43] (Figure 5.b). This necessitates the usage of longer columns in CEF and also to optimize the flow rate for achieving the best separation. The application of dynamic crystallization enables the use of higher cooling rates which is the principle reason for faster analysis by CEF compared to TREF and CRYSTAF. Monrabal et al.[44-47] compared the CCD based characterization of polyolefins by CEF with that by adsorption based techniques like high temperature liquid adsorption chromatography (HT-LAC).

In general, crystallization based techniques are being used routinely to determine the CCD of polyolefins. However, there are two major limitations of the technique that necessitate the finding of fundamental alternatives. The first limitation arises from co-crystallization which makes quantitative separations of blends difficult[48]. Secondly, as these techniques are based on the principle of crystallization, they cannot be applied to polymers with a lower degree of crystallinity. This was shown by Wild[29,49] and Kelusky[28] who analyzed the CCD of ethylene/vinyl acetate (EVA) statistical copolymers containing 9-42 wt.-% VA by TREF and found that copolymers with higher VA content are fully amorphous and thus could not be separated by TREF or CRYSTAF. For statistical copolymers of ethylene and 1-octene the range of separation via CRYSTAF has been found to be in the range 0 – 27 wt. -% (or 0 – 9 mol. %) of 1-octene content[44, 46]. This range may be increased by applying cryogenic techniques, but the freezing point of the solvent acts as a limiter. These limitations provided the driving force for the development of high performance liquid chromatography (HPLC) as an alternative method for CCD determination of polyolefins.

5.2 High-performance liquid chromatography (HPLC)

High performance liquid chromatography (HPLC) has been applied as a fast and selective separation technique to determine the MWD and CCD of polymers soluble at room temperature for many decades. In HPLC the macromolecules are separated based on different retention times as they pass through a chromatographic system comprising of a specific stationary and mobile phase. Different retention times of the individual components are caused by differences in the partitioning equilibrium between the stationary phase and the mobile phase[50]. The equilibrium can be expressed by the partitioning coefficient, K_d[51], given by Eq. 5:

$$K_d = \frac{C_{SP}}{C_{MP}} \tag{5}$$

Where, C_{SP} and C_{MS} are the concentrations of the analyte in the stationary phase and mobile phase, respectively.

Thermodynamically, K_d is related to the difference in Gibbs free energy of the analyte in both the mobile and the stationary phase[52, 53]. The difference between the enthalpic and entropic contributions results in a change of the Gibbs free energy (ΔG) as shown in Eq. 6:

$$\Delta G = \Delta H - T\Delta S = -RT \ln K_d \quad (6)$$

Eq. 6 rearranges into Eq. 7:

$$\ln K_d = \frac{-\Delta G}{RT} = \frac{-\Delta H + T\Delta S}{RT}$$
$$K_d = \exp(\Delta S / R - \Delta H / RT) \quad (7)$$

Where, R = universal gas constant,

T = the absolute temperature,

ΔH and ΔS are the changes in enthalpic and entropic contributions, respectively.

ΔH is the overall change in enthalpy from different attractive or repulsive interactions of the macromolecules with both the stationary and the mobile phase. ΔS is the overall change in entropy of the macromolecules arising from differences related to the hydrodynamic volume as they are excluded or enter the pores[54, 55] of the stationary phase. The enthalpic and entropic contributions in a chromatographic separation can be controlled by the choice of the stationary and mobile phase and the temperature. Based on the enthalpic and entropic contributions, HPLC separations can be classified into size exclusion chromatography (SEC), liquid adsorption chromatography (LAC) and liquid chromatography at critical conditions (LCCC). The thermodynamics of these chromatographic modes is shown in Table 3.

Table 3: Thermodynamics in different HPLC modes

Chromatographic mode	Thermodynamics
SEC	$\Delta H = 0$, $K_d = \exp(\Delta S/R)$
LAC	$\Delta S = 0$, $K_d = \exp(-\Delta H/RT)$
LCCC	$\Delta H = T\Delta S$, $K_d = 1$

5.2.1 Size exclusion chromatography (SEC)

SEC separates macromolecules based on differences in their hydrodynamic volume in a mobile phase. The variation in the hydrodynamic volume leads to differences in the exclusion of the macromolecules from a porous non-interacting stationary phase. Silica or semi-rigid (highly cross-linked) organic gels with a well-defined pore size distribution have been widely used as stationary phase. The mobile phase chosen is a thermodynamically good solvent for the polymer to prevent non-exclusion effects e.g., interactions between the stationary phase and the macromolecules[56]. In SEC a macromolecule entering the pore of the stationary phase experiences a loss of entropy according to its hydrodynamic volume in the mobile phase. This loss of entropy translates into different retention times for eluting macromolecules. Macromolecules with larger hydrodynamic volume experience a greater loss in entropy and elute earlier compared to smaller ones[57, 58]. Ideally, in SEC there should be no enthalpic contributions ($\Delta H = 0$), and Eq. 7 then changes to Eq. 8:

$$K_d = K_{SEC} = e^{\frac{\Delta S}{R}} \tag{8}$$

As $\Delta S < 0$, K_{SEC} ranges from 0 to 1, with $K_{SEC} = 0$ for macromolecules having a hydrodynamic volume larger than the largest pore volume (exclusion limit) and $K_{SEC} = 1$ for small macromolecules which can access the entire pore volume (separation limit). The retention times can be calibrated using narrow disperse standards of known MW. This calibration can then be applied to extract information about MW, MWD and dispersity (Đ) of unknown polymers samples.

However, in case the calibration standards are not chemically identical to the sample, the obtained MW, MWD, and Đ of the sample can be expressed only as a relative value. This problem can be solved by attaching a MW sensitive detector e.g., multi-angle laser light scattering (MALLS)[59, 60] which enables to determine the absolute MW.

Mostly, two averages of MW are determined from the MWD of a polymer[53]. These are the number average MW (M_n) and the weight average MW (M_w) and their definitions are given by Eq. 9-11:

$$M_n = \frac{\sum_{i=1}^{\infty} N_i M_i}{\sum_{i=1}^{\infty} N_i} \quad (9)$$

$$M_w = \frac{\sum_{i=1}^{\infty} N_i M_i^2}{\sum_{i=1}^{\infty} N_i M_i} \quad (10)$$

$$Đ = \frac{\overline{M}_w}{\overline{M}_n} \geq 1 \quad (11)$$

Where, N_i = the number of chains of the molecular weight M_i of a polymer sample.
Đ is calculated from the ratio of M_w to M_n. As per definition M_w is always equal or larger than M_n, Đ has a value ≥ 1.

Various detectors have been used with SEC for the characterization of polymers. A refractive index (RI) detector has been preferred for measuring the concentration of polymer eluting from the columns (SEC/RI). More recently, infrared (IR) spectroscopy has gained acceptance as concentration-sensitive detector for SEC (SEC/IR). The main advantage IR shows over the RI detectors are a comparatively more stable baseline and lower sensitivity to temperature fluctuations which is particularly important for high temperature applications. Additionally, information about the chemical composition of the eluting fractions is accessible.

Semi-crystalline polyolefins require elevated temperatures (above 100 °C) for dissolving, and this led to the development of high temperature SEC (HT-SEC)[57,61,62]. A HT-SEC column set comprises multiple columns connected in series that fulfill the necessary pore size distribution according to the sample being analyzed. The stationary phase of choice is cross-linked poly (styrene/divinylbenzene), whereas the routinely used mobile phase is TCB[61]. HT-SEC has also been applied to analyze the distribution of LCB in polyolefins by coupling it to specific detectors. The presence of LCB makes the macromolecule more compact compared to a linear one i.e., the hydrodynamic volume is smaller for the LCB containing one compared to the linear equivalent. This effect may be observed by applying a viscometer (VISC) and/or light scattering (LS) detector. A viscometer detects the presence of LCB by comparing the resultant

differences in their intrinsic viscosity, and a LS detector determines the LCB content by comparing the radius of gyration (R_g) of a branched and a linear macromolecule with similar MW. Both detectors can be coupled online to HT-SEC e.g., HT-SEC/RI-VISC, HT-SEC/LS or HT-SEC/RI-VISC-LS, to analyze the LCB distribution along the MWD of polyolefins. The triple detector system HT-SEC/RI-VISC-LS is becoming increasingly common for unraveling the molecular heterogeneities of polyolefins[61]. HT-SEC has also been applied to determine the distribution of SCBs along the MWD in olefinic copolymers by coupling it with Fourier transform infrared (FTIR), offline methods via a LC transform[63] or online with a heated flow cell[64, 65].

5.2.2 Liquid adsorption chromatography (LAC)

LAC has been widely used to separate polymers which are soluble at ambient temperatures according to their composition. The separation is driven by enthalpic interactions between the macromolecules and the stationary phase in the presence of an appropriate mobile phase and temperature. The thermodynamics behind an ideal LAC separation can be represented by Eq. 12:

$$K_d = K_{LAC} = e^{\frac{-\Delta H}{RT}} \qquad (12)$$

From Eq. 12 it can be observed that K_{LAC} depends on ΔH and the temperature. Larger macromolecules are able to achieve better contact with the surface of the stationary phase and consequently interact more strongly with the stationary phase and elute later[52]. An LAC experiment can be conducted with or without the presence of a gradient (with regard to mobile phase or temperature). To differentiate the two, LAC experiments with gradient will be termed gradient-LAC. In LAC the polymers are separated solely according their interaction with the stationary phase in the presence of an isocratic mobile phase at constant temperature i.e., isothermally. However, the strength of interaction between the polymer and the stationary phase is often too high to enable elution of the polymer i.e., the polymer remains adsorbed and elutes at high elution volumes. This can be overcome by gradient-LAC where the adsorbed polymer is desorbed by either applying a gradient in composition of the mobile phase or the temperature. The details behind the adsorption/desorption mechanism for both solvent and temperature gradient LAC will be explained in detail later.

The majority of published LAC separations of synthetic polymers has been realized at ambient temperature[50, 52]. The chromatographic separation of semi-crystalline polyolefins

however necessitates the application of higher temperature to achieve dissolution, and this led to the development of high temperature LAC (HT-LAC). A HT-LAC based method for the separation of polyolefins according to their CCD was not reported until recently due to the absence of a stationary phase that could reversibly adsorb polyolefins, which has been a long standing scientific challenge. In first investigations toward this goal Macko et al. showed the irreversible retention of linear PE and isotactic PP from dilute solution on zeolites as stationary phase in 2003[66-69]. Yet, as the adsorbed polymer could not be eluted from the zeolite and thus this approach was not a practical solution to the challenge. Subsequently, Heinz et al. separated a blend of HDPE and iPP by using silica-gel as stationary phase and a gradient of TCB→ethylene glycol monobutyl ether (EGMBE) by a mechanism of precipitation/dissolution. (EGMBE is a solvent for iPP and non-solvent for PE) in 2005[70-72]. However, the separation was significantly influenced by the MW of the polymer, which even overrides the effect of composition on the separation, and thus poses an obstacle towards a truly composition selective separation.

The breakthrough came with the discovery of porous graphitic carbon (PGC) as stationary phase[73-77] in 2009. The development of PGC for liquid chromatography which is commercially available as Hypercarb™ is credited to Knox et al.[78]. PGC constitutes of porous spherical particles with a surface that is crystalline and devoid of micro-pores. At the molecular level PGC is made up of graphitic sheets of hexagonally arranged carbon atoms linked by conjugated 1.5 order bonds, which are stacked together on top of each other[84]. The graphitic carbon atoms have fully satisfied valancies and hence in principle there are no functional groups on the surface of PGC. PGC is produced by first choosing a highly porous silica as template into which the carbon based material is impregnated with a phenol-formaldehyde mixture. This mixture is then heated to 80–160 °C to initiate polymerization. The size and porosity of the carbon particles produced depend upon the choice of the silica template. This is next pyrolyzed under inert atmosphere (nitrogen) at 1000 °C to produce a highly porous amorphous carbon. The silica template is then dissolved by passing a hot aqueous solution of sodium hydroxide. The porous amorphous carbon is next graphitized by thermal treatment at 2340 °C under inert atmosphere (argon) results in the removal of surface functional groups, rearrangements in the graphite structure and closing of micro-pores. Various reviews about PGC have been published by Knox and Ross[80], Leboda et al.[81] and West et al.[82].

As was briefly mentioned earlier gradient LAC can be conducted in two ways based on the type of gradient that drives the separation. When the separation is controlled by varying the mobile phase composition while keeping the temperature constant, the LAC method is termed as solvent gradient interactive chromatography (SGIC). On the contrary, if the separation is controlled by varying the temperature of the stationary phase at isocratic mobile phase composition the method is referred to as thermal gradient interactive chromatography (TGIC). These two methods may be applied both at ambient and high temperature. However, for the purpose of the thesis only the high temperature gradient techniques will be described as the focus of the thesis is on polyolefins.

5.2.2.1 High temperature solvent gradient interactive chromatography (HT-SGIC)

In HT-SGIC the macromolecules are separated by applying a gradient of mobile phase composition at isothermal conditions. According to the interaction behavior which polymers in solution exhibit with the stationary phase at specified experimental conditions the solvents can be classified as adsorption promoting and desorption promoting in nature. Typical adsorption promoting solvents for polyolefins are 1-decanol and n-decane, while ODCB and TCB[76, 77, 83] are desorption promoting. In HT-SGIC the sample is first dissolved and injected in an adsorption promoting solvent to adsorb the macromolecules onto a column packed with graphitic sorbents. The adsorbed sample is then selectively desorbed by applying a gradient from adsorption to desorption promoting solvent. The adsorbed macromolecules elute depending on the strength of adsorption with the sorbent, which in turn is a function of their composition and, to a subordinate extent, their MW.

Various carbon sorbents like PGC, carbon-clad zirconia, activated carbon and exfoliated graphite were tested by Chitta et al. with regard to their selectivity as stationary phase for HT-SGIC of PE and PP of varying tacticity[84]. HT-SGIC has been applied to separate blends of linear PE and PP of varying tacticity[77]. Statistical copolymers of ethylene/α-olefins and propylene/α-olefins were also separated based on the α-olefins content by HT-SGIC[76]. The separation in HT-SGIC was shown to be independent of MW above ~ 20 kg/mol by Ginzburg et al.[85] for HDPE in a 10 minute linear gradient of 1-decanol→TCB. The separation of polyolefins by HT-SGIC has been reviewed by Macko et al.[86].

The significant advantage of HT-SGIC over crystallization based techniques like TREF, CRYSTAF and CEF is the fact that it offers the capability to separate olefinic copolymers over the full range of comonomer content[76, 87]. Yet, HT-SGIC is limited with regard to the choice of detectors with the evaporative light scattering detector (ELSD) being the only option. The ELSD suffers from non-linear dependence of the detector signal on sample concentration as well as solvent composition[88, 89]. Even with careful calibration of its response, it is extremely difficult to obtain quantitative results with the ELSD, and this was the driving force for the development of high temperature TGIC (HT-TGIC) as an analytical tool for polyolefin separations.

5.2.2.2 High temperature thermal gradient interactive chromatography (HT-TGIC)

In HT-TGIC the macromolecules are selectively separated by applying a temperature gradient on the column packed with PGC as stationary phase using an isocratic mobile phase. The solvents commonly used as mobile phase are ODCB and TCB. In HT-TGIC the polyolefin is dissolved in the mobile phase of choice and injected into the column packed with PGC at high temperature. The sample is then adsorbed onto the PGC surface by reducing the temperature while maintaining a very slow (or even no) isocratic flow of the mobile phase. Subsequently, the sample is desorbed from the PGC by raising the temperature in a constant isocratic flow of the mobile phase.

Cong et al. reported the first HT-TGIC separation of polyolefins separating HDPE, PP of varying tacticity, and ethylene/1-octene (E/O) statistical copolymers in 2010[44, 73, 90-93] and showed that the separation becomes independent of the molecular weight above 22,500 g/mol[91]. Soares et al. evaluated the influence of sample concentration, cooling rate, cooling flow rate, heating rate and range of the temperature gradient on the resolution with PGC as stationary phase[92, 94]. Alternative substrates with an atomically flat surface such as boron nitride, molybdenum- and tungsten-sulphide were evaluated with regard to their potential as stationary phase for HT-TGIC, but the results were comparable to those with PGC[35, 36]. For HT-TGIC of polyolefins, the preferred mobile phases[44, 46, 90-92] have been ODCB and TCB. Phenol[46] and 1-chloronapthalene[95] are other solvents that have been applied as mobile phase for HT-TGIC.

HT-TGIC offers a significantly wider range of comonomer separation (0 – 33 mol. %) compared to crystallization based techniques (0 – 9 mol. %) but it is limited compared to HT-SGIC which offers separation in the complete range of comonomer content[96]. However, the important advantage of HT-TGIC over HT-SGIC technique is the option of using a variety of commercially available detectors such as IR, LS, and VISC.

5.2.3 Liquid chromatography at critical condition (LCCC)

Liquid chromatography at critical conditions (LCCC) is the third mode of chromatography which exists at the transition between SEC and LAC. LCCC is observed for a given combination of polymer/stationary phase/mobile phase at a specific temperature when the entropic term completely equals the enthalpic contributions i.e., $\Delta G = 0$. In LCCC the macromolecules with identical repeating units elute independent of their MW, and their elution behaviour is determined by subtle compositional or structural differences. The existence of LCCC was first theoretically proven by Belenkii et al.[97], Entelis et al.[98], and Skvortsov[99]. Since then, LCCC has been applied for:

a) Separation of block copolymer[53,100-107]
b) Determining the MW of constituent blocks in di- and tri-block copolymers[108, 109]
c) Separation of end-functionalized polymers based on the type of functional group[53, 98, 110,111].
d) Separation of polymers based on their architecture (for example, linear from star shaped, or linear from rings)[112-115]
e) Separations based on tacticity[116-119].

As of 2003 more than 250 chromatographic systems for LCCC conducted at ambient temperatures and their applications were reported[120].

As conditions for LAC of polyolefins were not known until recently, LCCC separations were limited to those olefin di-block copolymers for which critical conditions of non-olefinic block were known i.e., polystyrene in styrene/ethylene copolymers[109], and poly methyl methacrylate, PMMA, in MMA/ethylene copolymers[71].

5.2.4 Cross-fractionation techniques

The multitude of molecular heterogeneities in polyolefins has already been discussed. However, heterogeneities along different parameters are regularly inter-related and influence each other. Cross-fractionation techniques were developed to study these relationships. Coupling two orthogonal separations can also significantly enhance the separation efficiency as shown theoretically by Rittig et al.[121]. Various cross-fractionation techniques have been developed but only those applicable for polyolefins will be discussed as part of this thesis.

In polyolefins the two most important molecular heterogeneities are the CCD and the MWD, and, therefore, the majority of cross-fractionation techniques aim to couple different analytical techniques to determine the bivariate CCD x MWD. Technically, the coupling may be realized via stop-flow (offline) or in a continuous mode (online). The advantages of both approaches were reviewed by Fairchild et al.[122]. HT-SEC is routinely applied to determine the MWD of polyolefins[57, 62]. However, for determining the CCD different crystallization and, more recently, LC based techniques are used. Wild[52] first combined TREF and HT-SEC in an offline manner (TREF x HT-SEC) which was later on automated by Nakano and Goto[123]. Since 2007, Ortin et al.[124] have commercialized an automated TREF x HT-SEC instrument which has led to more consistent results compared to earlier constructed setups. Although TREF x HT-SEC offers the required comprehensive characterization a limitation is the fact that TREF can only be applied to well crystallizable samples[68, 125-127]. This spurred the application of HT-LAC for the determination of CCD and the development of two dimensional liquid chromatography (2D LC) techniques. Many successful 2D LC separations have been reported for polymers[128-136] at ambient temperatures. However, for polyolefins the development of two dimensional high temperature liquid chromatography (2D HT-LC) separations has been possible only recently[137, 138], with the combination of HT-SEC and HT-LAC in an online mode. The results of a cross-fractionation experiment are usually represented in a color coded contour plot. Similarly, in 2D HT-LC, the two different chromatographic modes of separation are denoted by the two axes of the contour plot, and the intensity of the peaks is shown by a color scale. Figure 6 shows a contour plot, where a blend consisting of HDPE and PP of varying tacticity and molecular weight and an ethylene/propylene (E/P) copolymer was separated by 2D HT-LC[138].

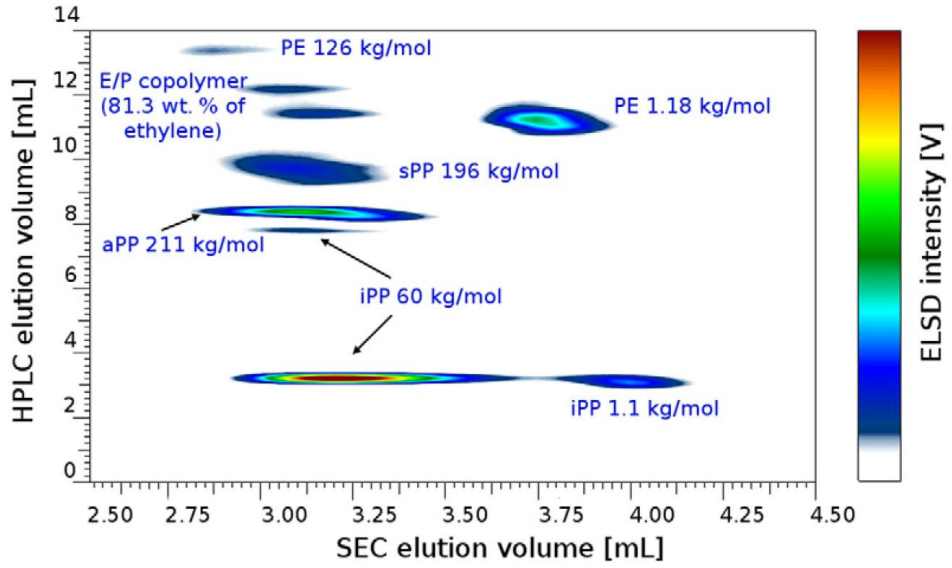

Figure 6: Contour plot obtained by 2D HT-LC of a blend of HDPE, PP of varying tacticity and E/P copolymers. From Ref. [138]

Since its development 2D HT-LC has been applied for the analysis for PE from different catalysts[137], EVA[139], ethylene/1-propene statistical copolymers[138], EPDM[138, 140], high impact PP[141], bimodal PE[85] and functionalized polyolefins[142].

5.3 Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) is a commonly used characterization technique for polymers. A DSC apparatus consists of sample positions or cells—one with the sample under investigation and the other as a reference, which is often an empty crucible or one filled with an inert material. Generally speaking in DSC the difference in the heat flow applied to increase the temperature of the sample with respect to a reference is measured as a function of temperature. Both the sample and the reference are maintained at nearly the same temperature throughout the experiment. The temperature program for a DSC analysis is designed such that the temperature of the sample holder increases with time. DSC can be applied to analyze any effect that is associated with a change in heat capacity or necessitate a heat flow.

5.3.1 DSC of polyolefins

In polyolefins DSC has been applied primarily to determine the temperatures of melting, crystallization and glass transition. Figure 7 shows the influence of the cooling rate on the crystallization behavior of LDPE as reported by Schick[143].

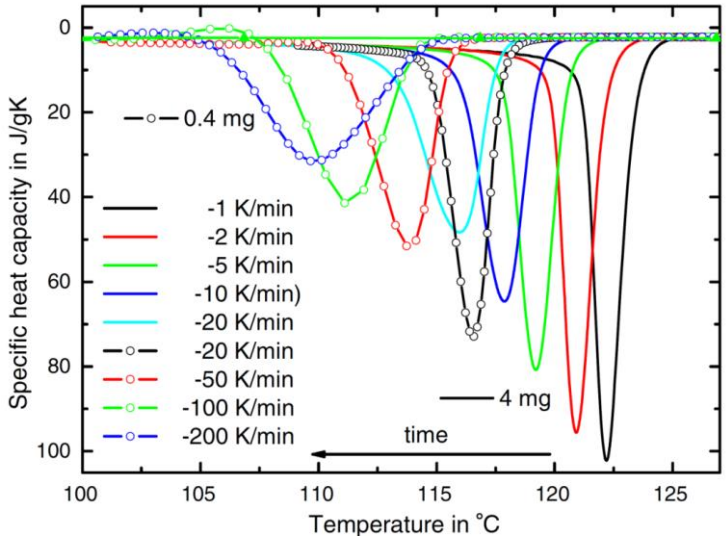

Figure 7: Cooling curves in the crystallization range of LDPE. Sample mass 4 mg in 25 mg aluminum pan for cooling rate up to -20 °C/min and of 0.4 mg in 2 mg aluminum foil for higher rates. Heat capacity is plotted downwards (Perkin-Elmer Pyris 1 DSC). From Ref. [143]

DSC techniques which enable fast cooling rates (up to 500 °C/min) (HyperDSC^{TM})[144,145] and, therefore, leading to higher sensitivity have been coupled to HT-HPLC separations with the help of a LC transform for thermal analysis of the eluting fractions from polyolefins[146, 147].

5.3.1.1 Solution DSC

DSC for polyolefins can also be carried out in a solvent and to differentiate this approach from regular DSC, it will be termed as solution DSC. Solution DSC has been applied to determine the CCD of polyolefins, and the results have been compared to those from CRYSTAF as both are based on the principle of crystallization[148]. However, compared to CRYSTAF the solution DSC experiments are limited in terms of their sensitivity which makes quantification problematic. Similar to CRYSTAF solution DSC also suffers from problems when it comes to accurate quantification due to co-crystallization effects. In fact these influences are stronger in solution DSC as it often requires high sample concentrations. The advantage of solution DSC is that it provides additional information about the composition of the polyolefins which are not found by the CRYSTAF[6]. Sarzotti et al.[148] have shown that while CRYSTAF fractionation of LLDPE is based on the crystallization of the longest ethylene sequence (LES), solution DSC experiments of LLDPE depend on the entire range of ethylene sequences. Therefore, for characterization of an LLDPE sample solution DSC is more responsive to the short chain branches in copolymers as compared to

CRYSTAF. This manifests in broader peaks of solution DSC compared to CRYSTAF as can be seen in Figure 8[148].

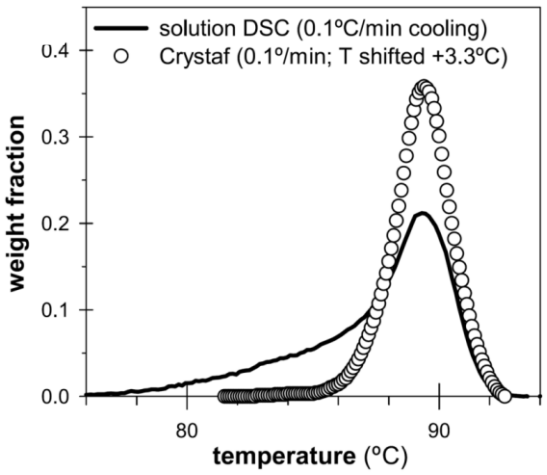

Figure 8: Comparison of weight fraction versus temperature from solution DSC and CRYTSAF for same metallocene polymers. From Ref.[148]

Solution DSC suffers from limitations in terms of resolution and co-crystallization, but can be complement CRYSTAF for providing vital microstructure information of polyolefin samples.

5.4 Nuclear magnetic resonance (NMR) spectroscopy

NMR spectroscopy is a powerful technique for chemical analysis having extensive applications in inorganic and organic chemistry, biochemistry, as well as medical sciences. NMR is based on the interaction of the magnetic properties of nuclei with an external magnetic field. In the absence of an external magnetic field the nuclei are aligned in a way that the magnetic dipoles are randomly oriented. However, when an external magnetic field is applied, the dipoles orient in different energy states based on an energy difference, ΔE, governed by Eq. 13:

$$\Delta E = \left(\frac{h\gamma}{2\pi}\right)\mathrm{B} \tag{13}$$

Where, γ = *gyromagnetic ratio*,

h = Planck's constant,

B = the strength of the external magnetic field.

The energy states with and without an external magnetic field for ^{1}H are shown in Figure 9 as an example.

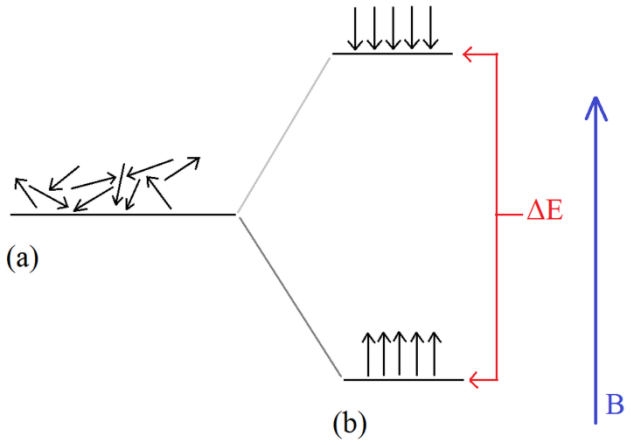

Figure 9: Representation of spins of ^{1}H atoms under (a) no magnetic field and (b) an external magnetic field B.

Apart from the nucleus, the applied magnetic field also interacts with the electrons spinning around the nucleus. The spinning electrons induce a secondary magnetic field which also influences the total magnetic field experienced by the nuclei. As the electron cloud is distributed unevenly in a molecule, the magnetic field experienced by a specific nucleus depends on its environment, and this delivers vital information about the molecular structure of the sample. Different nuclei are chosen for NMR spectroscopy based on requirement. Examples of nuclei applied for NMR are ^{1}H, ^{13}C, ^{15}N, ^{19}F, ^{31}P etc. Among these ^{1}H and ^{13}C are most commonly applied in NMR spectroscopy of polyolefins and will be focused on in greater detail.

5.4.1 NMR of polyolefins

For polyolefins NMR spectroscopy serves as an excellent technique for structure elucidation. A variety of structural information may be derived from a NMR spectrum with the help of *chemical shift* (ppm) which represents the ΔE relative to the reference proton (e.g., ^{1}H in Figure 9). A reference is commonly chosen, e.g., tetramethylsilane (TMS), whose chemical shift is assigned 0.00 ppm, and the different resonances are arranged according to the IUPAC recommended δ chemical shift scale[149]. The shielding effect from the surrounding electrons also influences the values of chemical shift. Even the same nucleus may exhibit different shifts based on differences in the electron cloud surrounding it, and this assists in deriving vital information about the microstructure of polyolefins. The factor that determines the

position of the signal in an NMR experiment is the magnetic field created by the other nuclei and the electrons in the molecule.

NMR spectroscopy of polyolefins requires elevated temperatures and solvents which have to be chemically stable and that don't evaporate at elevated temperatures. Additionally, for quantitative analysis of polyolefins the experimental parameters of NMR like probe tuning and relaxation delay need to be optimized[150]. NMR spectroscopy has become a routine technique for the characterization of polyolefins, and a few common applications are covered in the next section.

^{1}H and ^{13}C are the commonly applied nuclei for NMR spectroscopy of polyolefins. ^{1}H NMR has significantly higher sensitivities compared to ^{13}C NMR and is commonly applied for determining the chemical composition e.g., functional groups[151], end-groups[152], unsaturation[152-154] etc., that are present in too small quantities to be detected by ^{13}C NMR. ^{1}H NMR finds application as a great tool for quantification as it doesn't require additional calibration[150]. The area under the curve of each ^{1}H NMR signal is proportional to the number of equivalent protons creating the signal. Hence, by integrating the area under each curve the relative number of protons that constitute each curve can be quantified.

^{13}C NMR is the preferred technique for investigating the microstructure of polyolefins. The larger spectral width (~ 20 times) of ^{13}C NMR compared to ^{1}H NMR enables quantification of the microstructure of polyolefins. ^{13}C NMR has been successfully applied to determine microstructural information such as tacticity[156], inverse insertion[156] and comonomer sequence distribution[157]. ^{13}C NMR has also been applied to quantify SCB[158] and LCB[159-161] content in PE. The peak assignments for ethylene/1-octene copolymers (E/O) were reported by Qiu et al.[162]

5.4.1.1 Thermal gradient NMR (TG-NMR)

^{1}H NMR may also be measured at different temperatures either separately or with the help of a temperature array to analyze the chemical composition of molecules as the temperature inside the NMR tube is varied and for analyzing dynamic processes like hindered bond rotations and conformational ring changes, or kinetics of chemical reactions[163]. Zhou et al.

first applied this concept to polyolefins and used thermal gradient NMR (TG-NMR) for the analysis of unsaturation in polyolefins[152, 164]. The changes in the signal corresponding to the chemical composition e.g., unsaturations of a representative E/O copolymer in solution at different temperatures is shown in Figure 10 as reported by Zhou et al.[152]

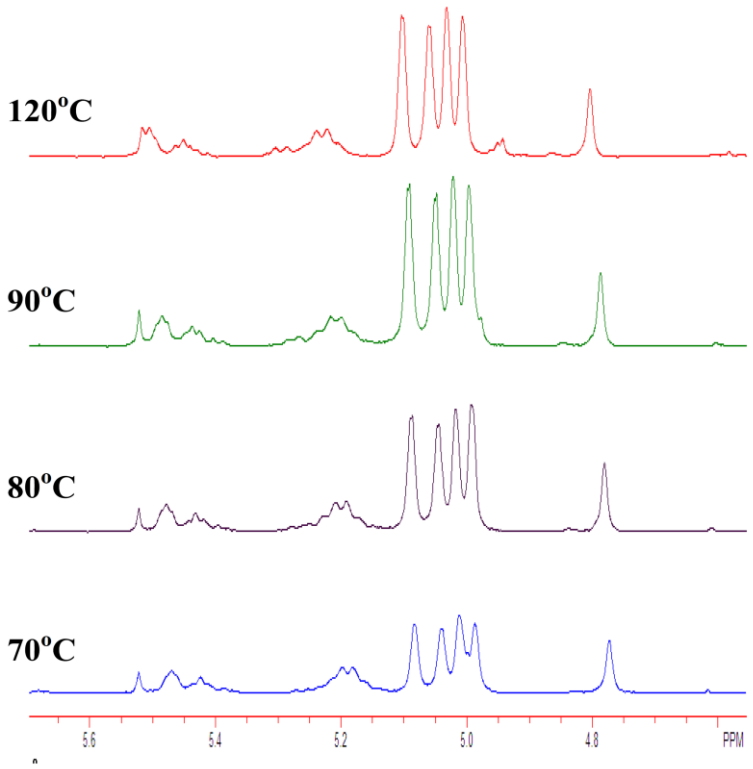

Figure 10: ^{1}H NMR from TG-NMR of E/O copolymer in the temperature range 120 → 70 °C in 10 °C steps. Focused on chemical shift range: 5.8 – 4.6 ppm. From Ref.[152]

TG-NMR of polyolefins is conducted by varying the temperature of the NMR sample over a specific range in a step wise manner (e.g., 120 → 70 °C, 10 °C steps in Figure 10) and analyzing the corresponding ^{1}H NMR spectrum at each step. The temperature variation common in a TG-NMR experiment may also effect the tuning of the probe which necessitates the usage of an inert reference standard. The reference can be added internally to the sample solution or externally with the help of a coaxial insert as shown in Figure 11.

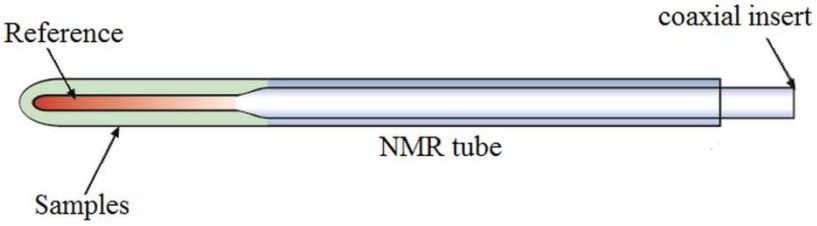

Figure 11: NMR tube with external reference in a coaxial insert

6. Results and Discussion (Cumulative)

HT-LAC has emerged as a fast and powerful fractionation technique to separate polyolefins with regard to their composition and microstructure. Carbon based sorbents have lately shown an outstanding selectivity as a stationary phase for this purpose. An important criterion when choosing the carbon based stationary phase for a particular separation is the chromatographic selectivity. Therefore, it is necessary to understand the fundamentals behind this selectivity which forms the motivation behind the current research.

The results of this research are divided into five parts: The first part shows the development of a new method to separate and identify oligomers in HDPE with the help of HT-SGIC. In the second part a multiple injection method is developed with the aim to enhance the signal intensity in HT-SGIC which can be adapted to improve the detection in 2D HT-LC separations. The third part shows the development of the HT-LCCC of polyolefins using PGC as stationary phase and binary solvent systems as mobile phase. The fourth part stems from HT-LCCC and utilizes binary solvent systems to improve the resolution in the separation of statistical copolymers of ethylene and 1-octene, with HT-TGIC. The research work is then rounded off with a study of the interactions between the macromolecules and nanographite as model for carbon based sorbents in the presence of a solvent. For this purpose suitable parameters for TG-NMR were developed, and HT-TGIC, CEF and solution DSC were used as complementary techniques.

6.1 Separation and identification of oligomers in HDPE by HT-SGIC

n-Alkanes are an important ingredient of waxes, oils, gasoline and a by-product in polyolefins. The separation and identification of n-alkanes are therefore of concern for polyolefin producers as they may have a significant impact on both the processability and end-use properties. Accurate identification of these may also be helpful to evaluate catalyst/process performance. Traditionally used gas chromatography (GC) and SEC-based methods may need certain extraction or pre-concentration steps, which tend to be time-consuming and are prone to handling errors.

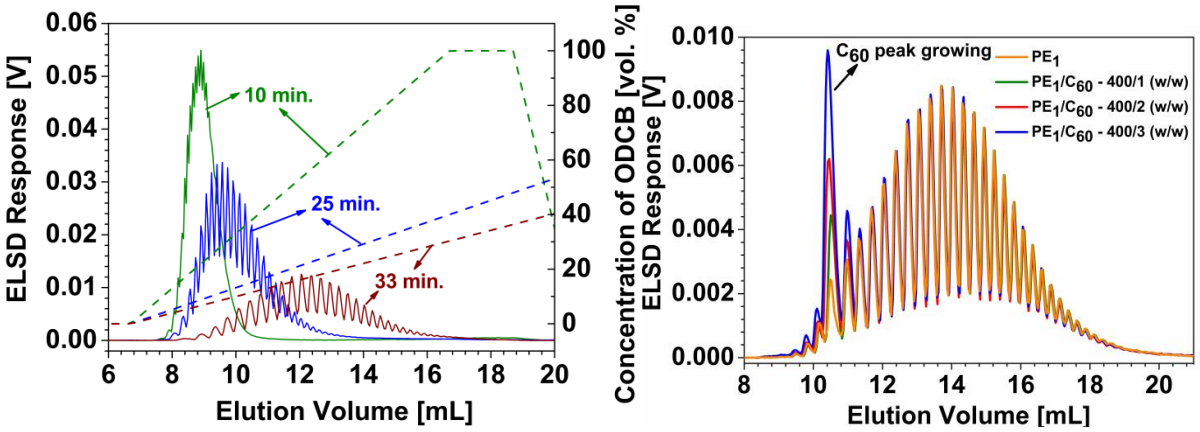

Figure 1: a) Chromatogram of HDPE (M_w 1 kg/mol) with Hypercarb™ at 160 °C. Eluent: n-decane→ODCB with different gradients depicted as dotted lines. b) Overlaid chromatogram with different wt. ratio of n-C_{60} doping.

This study shows a novel method to separate and identify n-alkanes in HDPE using HT-SGIC. Thus, n-alkanes in the range of C_{18}-C_{160} can be separated using PGC (commercially available as Hypercarb™) as stationary phase at specific chromatographic conditions. The separated alkanes were identified by doping the eluent with alkane standards and also by using MALDI-TOF as a reference technique. As a proof of concept, alkanes in an industrially-produced HDPE (M_w = 70 kg/mol) were analyzed. The key benefits of this approach are that no prior extraction is required and an excellent resolution.

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One-Step Method for Separation and Identification of *n*-Alkanes/Oligomers in HDPE Using High-Temperature High-Performance Liquid Chromatography

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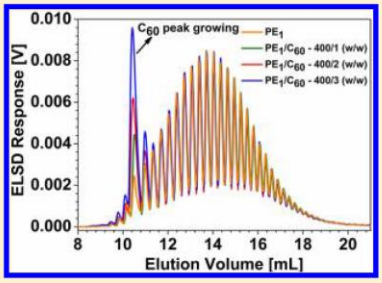
ABSTRACT: *n*-Alkanes are often an important ingredient of waxes, oils, gasoline, and a byproduct in polyolefins. Separation and identification of alkanes in commercial high-density polyethylene (HDPE) are of vital importance from various points of view. Currently used chromatographic techniques require extraction and laborious preconcentration. Porous graphite Hypercarb as a stationary phase in high-performance liquid chromatography (HPLC) in combination with a mobile phase gradient *n*-decane → 1,2-dichlorobenzene (ODCB) enables a selective separation of C_{40}−C_{160} *n*-alkanes at temperatures between 100 and 160 °C. Thus, it is possible to resolve the individual alkanes in HDPE of 1 kg/mol. An unambiguous assignment of the individual homologues in the chromatogram was possible by doping the HDPE with a C60 standard, and the results were also confirmed by MALDI TOF. Using this method, the presence of alkanes in a HDPE sample with a weight-average molar mass of 70 kg/mol could be shown. *n*-Hexane as isocratic mobile phase enables to separate and identify *n*-alkanes in the range C_{18}−C_{36} in a mixture at a temperature of 50 °C while alkanes with lower carbon numbers are not detected with the evaporative light scattering detector used in this study. The newly developed HPLC system allows separation and identification of alkanes in model blends as well as in high molecular weight HDPE without any prior extraction and work-up. The upper limit of detection with regard to carbon number is superior to the traditionally used gas chromatography.



INTRODUCTION

Alkanes represent an important class of compounds, as a key ingredient of waxes, oils, and gasoline or as a minor component in HDPE. Separation and identification of alkanes in waxes and commercial HDPE have therefore always been of extreme importance for the polyolefin industry. Chromatography has traditionally been used to fulfill this requirement, and both gas (GC)[1,2] and liquid chromatography (LC) have been used for this purpose. GC has an upper limit when separating alkanes of about 90−100 carbons, and resolution decreases when approaching this.[1,2] Separation by LC can be achieved via three fundamental modes, namely size exclusion (size exclusion chromatography, SEC), interaction (liquid adsorption chromatography, LAC), and liquid chromatography at critical conditions (LCCC). LCCC separates macromolecules based on differences in their repeating units and cannot be used on *n*-alkanes or HDPE as they all have the same repeating unit. SEC has been extensively used to separate alkanes with limited resolution. Stationary phases with small pores have been most successful and make it possible to separate alkanes from C_5 to C_{150}.[3−16,3,4,7,8,12,14,15] Silica gel[6,10] or porous glass[7] has been used as stationary phase for SEC-based separation of alkanes. LAC-based separations have been realized by using extremely weak eluents and at room temperature to promote adsorption on silica gel,[17−19] reversed phase silica gel,[20−30] alumina,[31] or zeolites.[32] GC which has excellent resolution and SEC using small pore size stationary phases with its longer range of separation have been the preferred techniques to separate alkanes. Möckel et al.[33] indicated that *n*-alkanes in the range of C_6 to C_{15} are stronger retained on a column packed with porous graphitic carbon (PGC) than on silica gel C18, when using methanol as eluent. Alkanes are homologues to PE, and recently PGC has been used successfully as stationary phase for LAC of HDPE with both solvent gradient[34−39] and temperature gradient (TGIC).[40] Using a Hypercarb column in TGIC mode, alkanes were observed in low molar mass HDPE (M_w 0.7 and 1 kg/mol).[41] However, the resolution was not sufficient to accurately identify individual alkanes.

The separation and identification of alkanes are of major concern for polyolefin producers as the presence of even small amounts of these may have a large impact on both the processing and application properties of the final product. In the same way, identification of oligomers is of pivotal interest when it comes to evaluate catalyst performance. Another need to identify and quantify oligomers arises from polyolefin applications in food and packaging, where some alkanes migrate to the film surface and thus come in contact with the contents. Traditional GC- and SEC-based methods used to separate alkanes need extraction or preconcentration before the

Received: June 3, 2013
Published: July 29, 2013

separation and identification can be carried out, and it is a time-consuming and painstaking process to ensure proper extraction of oligomeric components from the bulk material. In this paper a one-step liquid chromatographic approach for the separation and identification of alkanes in HDPE is reported.

EXPERIMENTAL SECTION

Solvents and Samples. *n*-Decane and 1,2-dichlorobenzene (ODCB) were used as received for solvent gradient measurements. *n*-Hexane was used for isocratic measurements without further purification. The solvents were obtained from Merck, Darmstadt, Germany.

n-Tetracontane (C_{40}), *n*-pentacontane (C_{50}), and *n*-hexacontane (C_{60}) were purchased from Sigma-Aldrich, Netherlands. *n*-Alkanes C_{18}−C_{36} were obtained from Dr. Denayer (Department of Chemical Engineering, Vrije Universiteit Brussel, Belgium). HDPE standards of weight-average molar mass (M_w) 1 and 2 kg/mol were obtained from Polymer Standards Service, Mainz, Germany. A HDPE sample with a M_w of 70 kg/mol was obtained from the Dow Chemical Company, Freeport, TX.

Polymer samples were prepared by dissolving them in the respective mobile phases at 2 mg/mL for the solvent gradient experiments and 1−2 mg/mL for the isocratic experiments. The samples were dissolved at different temperatures (50, 100, 130, or 160 °C) for various periods of time (1−3 h) depending on the sample's respective molar mass.

High-Temperature Liquid Chromatography. All measurements were conducted on a PL XT-220 high-temperature liquid chromatograph (Agilent Technologies, Santa Barbara, CA). Sample injection was performed by a robotic sample handling system, PL-XTR, also from Agilent Technologies. A sample loop of 50 μL was used. A constant flow rate of 1 mL/min and a constant temperature (130 or 160 °C) were maintained for all experiments. A Hypercarb column, 4.6 × 100 mm^2 IDxL (Thermo Fisher Scientific, Dreieich, Germany), containing spherical particles of porous graphite with an averaged particle diameter of 5 μm was used. An evaporative light scattering detector (ELSD), model PL-ELS 1000 (Polymer Laboratories), was used. The nebulizer temperature and the evaporation temperature were at 160 and 260 °C (for *n*-decane → ODCB), respectively, or at 50 and 80 °C (for *n*-hexane) with a nitrogen flow rate of 1.5 L/min in all cases. Data collection and processing was done using WinGPC-Software from Polymer Standards Services, Mainz, Germany.

The total delay of the chromatographic system was calculated to be 3.7 mL using the method of Ginzburg et al.[42] The delay volume was measured as the total volume between the pump and detector. The composition of the mobile phase was generated by a gradient pump (Agilent, Heilbronn, Germany) according to one of three programs (Table 1). Based on the delay volume of 3.7 mL (i.e., 3.7 min at a flow rate of 1 mL/min), the composition of the mobile phase in the cell of the ELSD was calculated (Table 1).

Matrix-Assisted Laser Desorption/Ionization Time of Flight (MALDI TOF). The MALDI TOF measurements were carried out on AXIMA TOF^2 mass spectrometer (Shimadzu Biotech, Manchester, UK). A nitrogen laser (337 nm) was used for ionization. The instrument was set to the positive linear mode.

The samples for the MALDI TOF experiments were prepared in three layers. The first layer was 1 μL of 0.1 M matrix solution: retinoic acid in tetrahydofuran. The second layer consisted of 0.5 μL of saturated $AgNO_3$ in methanol, and the third layer was 1 μL of a polymer solution at a concentration of 5 mg/1 mL in ODCB.[43]

Table 1. Composition of the Mobile Phase in the Gradient Pump and Calculated Composition of the Mobile Phase in the ELSD

	linear gradient - time in pump					
desorption promoting solvent [vol %]	10 min		25 min		33 min	
0	0	0	0	0	0	0
0	3.0	6.7	3.0	6.7	3.0	6.7
100	13.0	16.7	28.0	31.7	36.0	39.7
100	15.0	18.7	30.0	33.7	38.0	41.7
0	17.0	20.7	32.0	35.7	40.0	43.7
0	30.0	33.7	45.0	48.7	60.0	63.7

RESULTS AND DISCUSSION

Reversible adsorption of HDPE in a PGC packed Hypercarb column has been investigated in detail using a 10 min linear solvent gradient 1-decanol → TCB (1-decanol → $TCB_{10\ min}$).[34−39] The peak shape for HDPE 1 kg/mol in this solvent/sorbent system indicated the presence of low molar mass species, but the resolution was very poor (Figure 1).

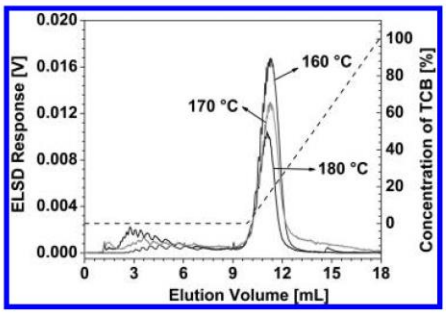


Figure 1. Overlay of chromatograms of HDPE M_w of 1 kg/mol. Injection loop: 50 μL. Sample concentration: 2 mg/mL. Column: Hypercarb, 4.6 × 100 mm^2 IDxL. Flow rate: 1 mL/min. Eluent: 1-decanol → $TCB_{10\ min}$. Composition of respective mobile phase gradient in the cell of the ELSD is indicated in the figure with the dotted line.

To improve the separation between these small peaks, longer gradients of 25 min (1-decanol → $TCB_{25\ min}$) and 33 min (1-decanol → $TCB_{33\ min}$) were applied as specified in Table 1. Prolonging the gradient should provide more separation between the peaks and hence better resolution at the expense of signal-to-noise ratio. It was observed that 1-decanol and TCB, which have boiling points (bp) of 233 and 215 °C, respectively, show high noise levels in spite of the evaporation temperature in the ELSD being set at 260 °C, and this resulted in a poor signal-to-noise ratio. This in turn made it very difficult to realize the improvement in resolution achieved with a longer gradient. It has to be noted that the elevated noise is not noticeable in routine HPLC experiments that are typically conducted using 10 min gradients, as the sample peaks are of much higher intensity so this slightly higher noise level is negligible for those calculations. Another interesting phenomenon which will be described in detail later on in the paper is the ELSD's inability to detect alkanes lower than C_{50} when its evaporation temperature is set at or above 260 °C.

n-Decane (bp 174 °C) and ODCB (bp 180 °C) were chosen as components of the solvent gradient to improve detectability and separation. With their lower boiling points, the ELSD could also be used at lower evaporation temperatures and thus detect alkanes lower than C_{50}. This gave an added advantage of using *n*-decane → ODCB and has been applied to increase the separation range further as compared to the traditionally used 1-decanol → TCB. This enhanced separation range with *n*-decane → ODCB, combined with a shallower gradient, should

give an extremely improved resolution for the separation of alkanes in PE.

Figure 2 shows the separation of HDPE with M_w of 1 kg/mol (PE_1) (1 kg/mol) with *n*-decane → ODCB at 160 °C by using

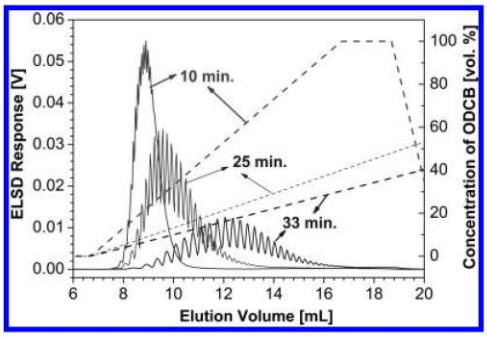


Figure 2. Overlay of HT-LC chromatograms of HDPE (M_w of 1 kg/mol). Injection loop: 50 μL. Sample concentration: 2 mg/mL in *n*-decane. Column: Hypercarb, 4.6 × 100 mm^2 IDxL. System temperature: 160 °C. Flow rate: 1 mL/min. Eluent: *n*-decane → $ODCB_{33\ min}$. Composition of respective mobile phase gradient in the cell of the ELSD is indicated in the figure with the dotted lines.

gradients of varying length (Table 1). The single HDPE peak is separated into individual alkane components. Using 1-decane → $TCB_{33\ min}$, almost baseline separation was observed, although the ELSD response of all peaks became lower and broader as desorption was spread over a longer elution range due to the increase in gradient duration. This clearly demonstrated a significant improvement in the resolution with *n*-decane → $ODCB_{25\ min}$ and *n*-decane → $ODCB_{33\ min}$.

The identification of each peak is a legitimate question. To answer this, HDPE 1 kg/mol was doped with a very small amount of n-C_{60} standard, and the peak intensities of the resulting chromatograms were compared with those of the HDPE sample without doping. Figure 3 shows the HT-LC chromatograms of HDPE 1 kg/mol and those of PE_1 doped with C_{60} in ratios of 400/1, 400/2, and 400/3 (w/w). When compared with the neat HDPE sample, it can be observed from Figure 3 that upon increase of the doping level the first six peaks' ELSD signal increases. This increase is most pronounced

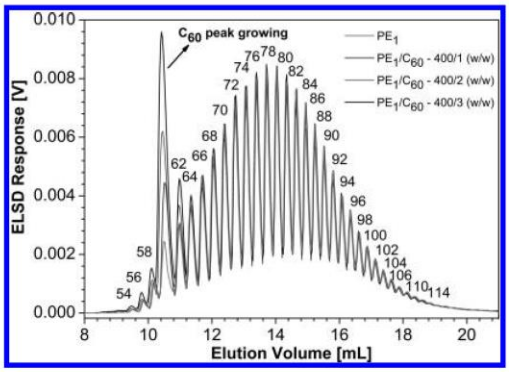


Figure 3. Overlay of HT-LC chromatograms of HDPE 1 kg/mol (PE_1) doped with n-C_{60} at three different levels. Column: Hypercarb, 4.6 × 100 mm^2 IDxL. System temperature: 130 °C. HPLC Flow rate: 1 mL/min. Eluent: *n*-decane → $ODCB_{33\ min}$. Sample concentration: 2 mg/mL.

for the fourth peak, which was hence assigned as the C_{60} peak for the separated alkanes. The remaining peaks' intensities all remain unaffected by the increase of the doping level. The increase in the peak height (millivolts) is tabulated in Table 2.

Table 2. Increase in ELSD Response with Increase in Amount of C_{60} Doping into HDPE 1 kg/mol (Obtained from Figure 2)

	ELSD response (mV)			
		PE_1/C_{60}		
peak (elution vol)	PE	400/1	400/2	400/3
1st peak (9.5 mL)	0.13	0.13	0.14	0.24
2nd peak (9.8 mL)	0.41	0.42	0.47	0.68
3rd peak (10.1 mL)	0.10	1.1	1.1	1.5
4th peak (10.4 mL)	2.4	4.4	6.1	9.5
5th peak (11.0 mL)	2.9	3.0	3.6	4.5
6th peak (11.3 mL)	3.6	3.6	3.6	4.0

HDPE 1 kg/mol is prepared by fractionating narrow M_w regions from a parent sample to match the required molar mass specification. It is therefore expected to contain even numbered *n*-alkanes (i.e., 60, 62, 64, etc.), while waxes of natural origin may contain continuously numbered *n*-alkanes (i.e., 60, 61, 62, 63, etc.). However, whether the separated peak belongs to a continuous carbon-numbered alkane or an even-numbered alkane cannot be simply derived from the doping method described above. To solve this problem, MALDI TOF using the method described by Guttman et al.[43] was conducted. A mass difference of 28 (Figure 4) was identified which corresponds to two methylene groups ($-CH_2-$).

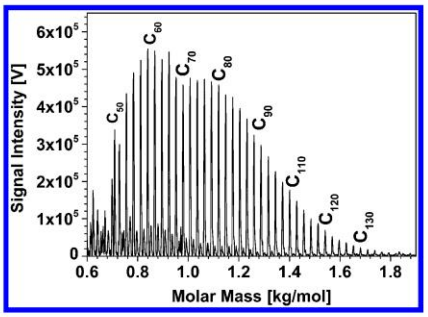


Figure 4. Mass spectrum obtained with MALDI TOF for HDPE 1 kg/mol. Distance between two consecutive major peaks is 28 g/mol.

This confirms that the alkanes are even-numbered. The presence of a series of low-intensity peaks between the higher intensity peaks in Figure 4 is due to fragmentation during the high-energy laser ionization experiments and is a common occurrence.[43] Thus, the individual peaks observed in the chromatogram (Figure 2) can be unambiguously identified as even numbered alkanes ranging from C_{50} (molar mass 702 g/mol) to C_{134} (molar mass 1878 g/mol) from Figure 4.

To further increase the separation range, a blend containing C_{60}, HDPE 1 kg/mol, and HDPE 2 kg/mol at a ratio of 400/35/12 (w/w) was analyzed in *n*-decane → $ODCB_{33\ min}$ (Figure 5). Alkanes from C_{54} to C_{160} were identified and separated to almost baseline resolution in the lower range under these conditions.

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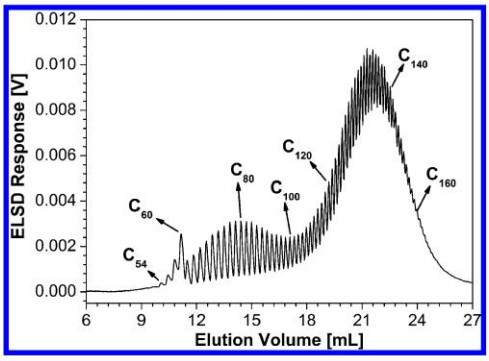

Figure 5. Chromatogram of a blend consisting of HDPE 2 kg/mol, HDPE 1 kg/mol, and C_{60} (400/35/12 wt ratio). Column: Hypercarb, 4.6 × 100 mm^2 IDxL. System temperature: 130 °C. Flow rate: 1 mL/min. Eluent: *n*-decane → $ODCB_{33\ min}$. Sample concentration: 2 mg/mL.

The identified alkanes can then be plotted according to their carbon number or molar mass versus elution volume, and this relationship can be used as calibration for similar HDPE samples (Figure 6). By comparing the elution volume with this

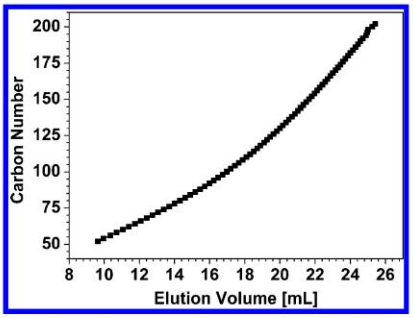

Figure 6. Carbon number versus the elution volume for *n*-alkanes (data from Figure 5).

calibration, alkanes present in similar and even higher molar mass commercial HDPE can be identified as will be shown in this paper later.

Column length is a factor which influences resolution in interactive chromatography. The separation of alkanes in HDPE 1 kg/mol using *n*-decane → $ODCB_{33}$ on Hypercarb of varying lengths was studied for the influence of column length on resolution (Figure 7). Because of the larger pore volume in longer columns, the column dwell volume increases; hence, the peaks are shifted to higher elution volume (Figure 7a). To facilitate the comparison of column length, the three chromatograms were shifted and normalized to same maximum height of the peak (Figure 7b). An increase in column length from 100 to 250 mm improves the resolution of the separated alkane peaks. However, further increasing the length to 50 cm leads to no more improvement. In fact, the resolution decreases (Figure 7b). These observations point toward a limit to improvement that can be achieved by increasing the column length: Using a longer column increases the efficiency of the separation; however, it also induces an increased band broadening. The distance (volume) between the individual alkanes is, however, not affected by the column length (Figure 7); i.e., it depends entirely upon the type of desorption gradient applied.

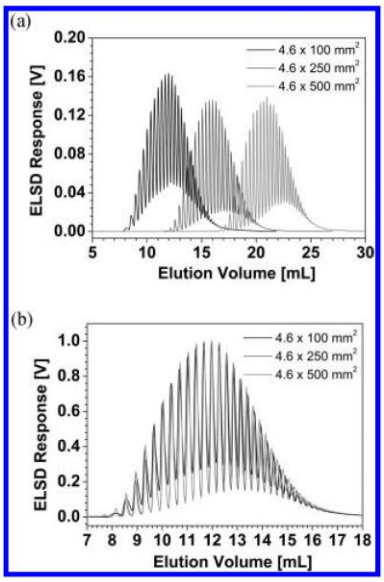

Figure 7. Chromatograms of HDPE 1 kg/mol (a) using Hypercarb of dimensions 4.6 × 100 mm^2, 4.6 × 250 mm^2, and 4.6 × 500 mm^2 IDxL. System temperature: 130 °C. Flow rate: 1 mL/min. Eluent: *n*-decane → $ODCB_{33}$. Sample concentration: 2 mg/mL. Overlay of chromatograms in (b) obtained after normalization and realignment of chromatograms shown in (a).

It was found experimentally that only oligomers with a carbon number >50 are detected at an evaporation temperature of 260 °C in the ELSD. This may be explained by the fact that alkanes below C_{50} evaporate along with the solvent at 260 °C and hence are not detected by the ELSD, as discussed earlier. However, the boiling point of C_{40} is 525 °C;[44] i.e., it should be impossible to evaporate this substance at 260 °C. But looking into the operation of an ELSD, it is known that a sample with a solvent is first nebulized into extremely fine droplets, which increase the surface area of the nebulized solvent.[45,46] Moreover, a large volume of nitrogen gas (1.5 L/min) is continuously passed through the detector cell which substantially improves the removal of the samples from the surface of the droplets. Taking these two factors into account, it may be speculated that the evaporation might take place at temperatures around 200−250 °C lower than the boiling points of the components of the mobile phase.

With 1-decanol → TCB the evaporation temperature of the ELSD has to be kept above their boiling points at 260 °C. However, by using *n*-decane → ODCB, it was possible to use the ELSD at an evaporation temperature of 190 °C to facilitate detection of alkanes down to C_{40} (Figure 8) in a PE standard with M_w of 0.74 kg/mol. Alkanes >C_{40} were identified by doping with C_{40} and C_{50}.

To further increase the separation range and include alkanes less than C_{40}, *n*-hexane was chosen as isocratic mobile phase. Figure 9 shows that *n*-alkanes C_{18}−C_{34} elute baseline separated from the Hypercarb column at 50 °C. *n*-Alkanes with lower boiling points, such as n-C_{18}, are not detected in the ELSD.

To have a good knowledge about the full range of alkanes present in polyolefin products is immensely important for industry as the presence of alkanes influences the performance of HDPE products, their processability, and other end-user applications. Figure 10a illustrates the chromatogram of such a

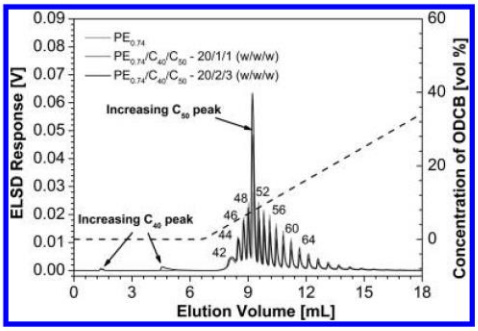

Figure 8. Chromatogram obtained after injecting a blend of PE 0.74 kg/mol (PE0.74), C40, and C50 of different composition (wt ratio). Column: Hypercarb, 4.6 × 100 mm^2 IDxL. System temperature: 100 °C. Flow rate: 1 mL/min. Eluent: *n*-decane → $ODCB_{33\ min}$. Composition of respective mobile phase gradient in the cell of the ELSD is indicated in the figure with the dotted line. Sample concentration: 2 mg/mL. ELSD Evaporation temperature: 190 °C.

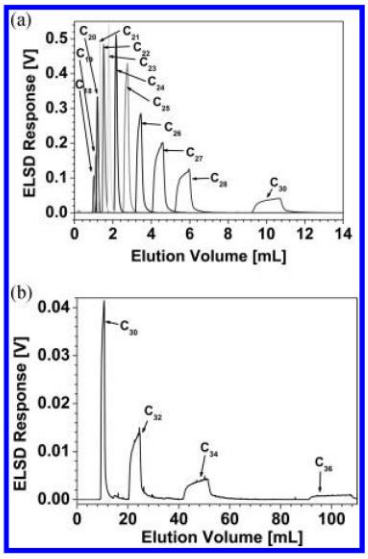

Figure 9. Chromatograms of *n*-alkanes in range of (a) C_{17}−C_{30} measured separately and (b) C_{30}−C_{36} measured as a model mixture. Column: Hypercarb, 4.6 × 100 mm^2 IDxL. System temperature: 50 °C. Flow rate: 1 mL/min. Eluent: isocratic *n*-hexane. Sample concentration: 2 mg/mL. ELSD evaporation temperature: 80 °C.

model HDPE sample (M_w = 70 kg/mol) in which a small peak at 9 mL elution volume was observed.

As was discussed earlier, the usage of longer gradient results in a lower response of the ELSD and a broadening of peaks. This is especially true for minority component of the sample, which are lower in concentration, like alkanes here in the HDPE sample. One solution to this challenge is to increase the height of this peak by repeatedly injecting into the column before starting the gradient elution. This approach may as well be substituted by using a higher concentration (if viscosity of sample solution is not an issue) or a larger injection loop. After injecting 10 times and focusing on the peaks at 9 mL elution volume, the presence of alkanes can be detected (Figure 10b). These particular alkanes can be identified by comparison of their retention volume with the calibration done on a similar system (Figure 6) or by doping with other alkane standards as

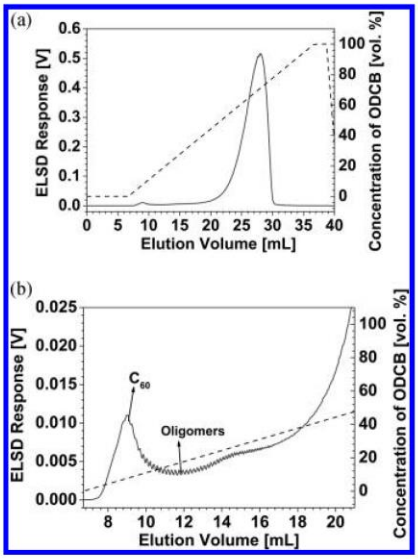

Figure 10. Chromatogram corresponding to HDPE (M_w = 70 kg/mol). Column: Hypercarb, 4.6 × 100 mm^2 IDxL. System temperature: 160 °C. The sample was injected 10 times. Flow rate: 1 mL/min. Eluent: *n*-decane → $ODCB_{33\ min}$. (a) Complete chromatogram. (b) Only part of the chromatogram is shown to assist visualization. Composition of respective mobile phase gradient in the cell of the ELSD is indicated in the figure with the dotted line.

has been shown in earlier done experiments (Figures 3, 5, and 8). As no separate extraction or preconcentration step is required, this test method provides a much faster feedback about the product than other chromatographic techniques like GC and SEC. Thus, it is a quick and robust method to probe the presence of alkanes in waxes as well as commercial HDPE.

■ CONCLUSION

A new chromatographic system was developed for the HPLC separation of *n*-alkanes, utilizing the pronounced improvement in separation of alkanes on PGC surface (Hypercarb) with *n*-decane → $ODCB_{33}$. The system Hypercarb/*n*-decane $OBCB_{33\ min}$ enables to separate *n*-alkanes in the range of C_{42}−C_{160} and by using Hypercarb/(isocratic) *n*-hexane the range can be further extended to C_{18}−C_{160}. Excellent separation with clear identification of individual peaks can be achieved up to C_{160}, although the resolution decreases with increase of number of carbons in alkanes. An unambiguous assignment of individual alkanes was possible by doping with a C_{60} standard and by using MALDI-TOF as reference technique. A calibration curve of carbon number vs chromatographic elution volume could be established. The advantage of this method is demonstrated with a commercial HDPE where alkanes up to C_{160} could be identified. In summary, this method has the clear advantage of providing a much faster and simpler alternative for separation and identification of alkanes, without a need for preconcentration and extraction steps such as those commonly used for GC and SEC methods.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research forms part of the research collaboration between Department of Material Analytics, Fraunhofer Institute, LBF, Darmstadt, and Dow Chemical Co. The authors thank to Ms. J. Beer (Fraunhofer LBF, Darmstadt) for realization of MALDI TOF measurements.

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6.2 Multiple injection method for improving detection in 2D HT-LC

For gaining a comprehensive understanding of the molecular heterogeneities in polyolefins apart from determining the MWD and CCD it is equally vital to establish the inter-relationship of both distributions. This need has spurred the development of cross-fractionation techniques like 2D HT-LC. In 2D HT-LC, a HT-LAC is coupled to a HT-SEC in an online manner to achieve a bivariate CCD x MWD separation of polyolefins. However, 2D HT-LC suffers from a low detector response due to the dilution of the sample fractions in the transfer step. This can be overcome by using stacked/multiple injections which leads to higher signal intensity.

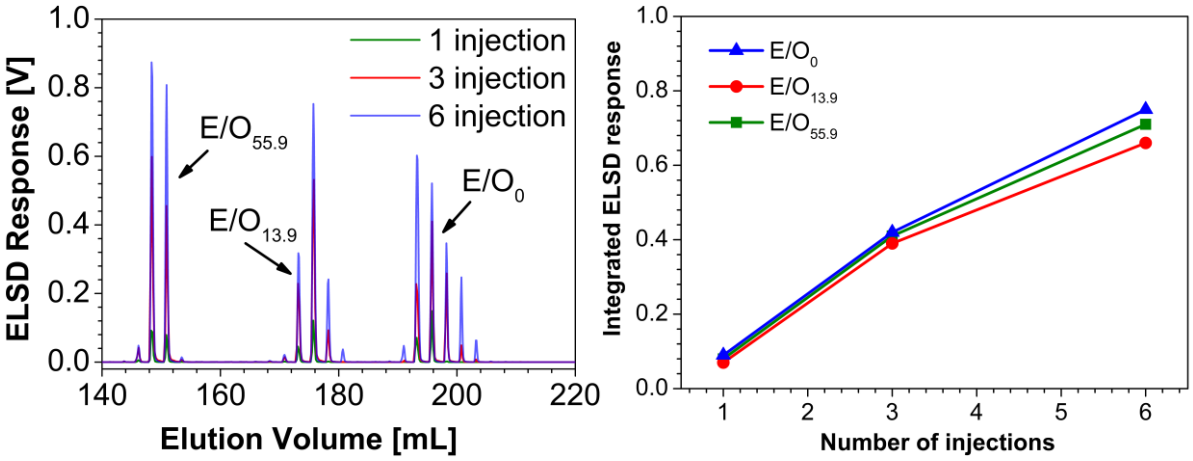


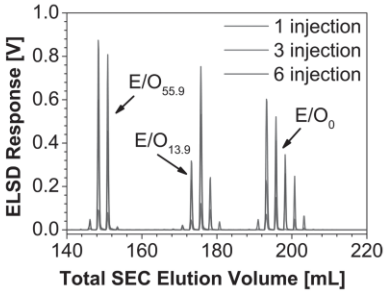
Figure 1: (a) Chromatogram overlay and (b) integrated ELSD response from 1:1:1 (wt.-%) blend of E/O_0, $E/O_{13.9}$ and $E/O_{55.9}$ separated by 2D HT-LC with varying numbers of injections.

In the developed method the sample solution is injected multiple times to first pre-concentrate the adsorbed sample on the carbon based stationary phase from an adsorption promoting solvent, and then desorbed in a single step by a gradient of a desorption promoting solvent to achieve higher signal intensities as shown by Figure 1. To demonstrate the applicability, model blends of E/O statistical copolymers were analyzed by 2D HT-LC using the newly developed method.

Multiple-Injection Method in High-Temperature Two-Dimensional Liquid Chromatography (2D HT-LC)

Dibyaranjan Mekap, Tibor Macko, Robert Brüll,* Rongjuan Cong, Willem deGroot, Albert Parrott, Wallace Yau

Comprehensively characterizing the relationship between the distributions with regard to chemical composition (CCD) and molar mass (MMD) of polyolefins is vital to establish structure–property relationships. Two-dimensional high-temperature liquid chromatography (2D HT-LC), which couples a high-temperature solvent gradient interactive chromatography (HT-SGIC) step for compositional separation with a high-temperature size exclusion chromatography (HT-SEC) step for MMD determination in an on-line manner is emerging as a tool of choice to satisfy this necessity. A serious problem commonly associated with multidimensional chromatography is the very low detector response (DR) due to the dilution in the HT-SEC step. Using higher sample concentrations or larger sample loops cannot address this appropriately because injections may become irreproducible, or poorly shaped peaks may result due to concentration effects. This paper shows that stacked injections (repeatedly injecting a polymer sample and then starting the desorption step) is a unique way to overcome these difficulties. 2D HT-LC analysis of blends of ethylene/1-octene copolymers using stacked injections proves that the DR can be significantly enhanced without co-elution of the blend components or overloading of the column.



1. Introduction

Molecular structure and heterogeneity of polymers play an important role in determining the properties of polymers. For polyolefins, molecular heterogeneity can be categorized to a large extent into the distributions with regard to molar mass (MMD) and chemical composition (CCD). High-temperature size exclusion chromatography (HT-SEC) has been used routinely to determine the MMD of polyolefins.[1,2] It is based on the principle that the extent to which macromolecules diffuse into the pores of a stationary phase depends on their hydrodynamic volume in a mobile phase. Crystallization-based techniques such as temperature rising elution fractionation (TREF),[3,4] Crystallization analysis fractionation (CRYSTAF)[3,5] and, more recently, crystallization elution fractionation (CEF)[6] have been used to analyze the CCD.

For synthetic polymer samples MMD and CCD are generally not independent, i.e., knowledge of their correlation is essential to establish structure↔property relationships. In response, Balke et al.[7,8] introduced the concept of two-dimensional liquid chromatography (2D-LC), which has been applied to numerous polymers, which are soluble at room temperature.[9–23] As a chromatographic separation of polyolefins according to composition has not been possible until recently multidimensional separations of polyolefins used a crystallization-based step (TREF) in the first dimension. Wild et al.[24] were the first to couple TREF

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Macromol. Chem. Phys. **2014**, *215*, 314–319

DOI: 10.1002/macp.201300649

with HT-SEC (TREF × SEC) in an off-line manner. Nakano and Goto[25] reported first the concept of automation in TREF × SEC, which has meanwhile been developed into fully automated TREF × SEC instrumentation.[26,27] However, TREF × SEC has limitations when characterizing samples of low or no crystallinity. The discovery of reversible adsorption of non-polar polyolefins on porous graphitic carbon (PGC) was the keystep for high-temperature solvent gradient interactive chromatography (HT-SGIC)[28–30] and thus finally opened the door for two-dimensional high-temperature liquid chromatography (2D HT-LC).[31,32] In 2D HT-LC, the polyolefin sample is first separated by HT-SGIC and the fractions are then transferred to HT-SEC as the second step. The effluent from the SEC column is detected by the means of an evaporative light scattering detector (ELSD) or infrared detector (IR). Since its development 2D HT-LC has been applied for the separation of PE, PP, ethylene/1-alkene copolymers,[33] functionalized polyolefins,[15] high impact PP,[34,35] and PE made from different catalyst types[32] or different process design.[36]

The emergence of 2D HT-LC as an important tool for polyolefin characterization has also brought with the need to increase sensitivity on the detection side for quantification. The high dilution (5–10 times, depending on the experimental parameters) of the analyte during the sample transfer between the chromatographic dimensions often results in a poor detector response (DR). As every copolymer is chemically more or less heterogeneous per se, this problem becomes severe in polymer analysis, as minor components will always be present, which may strongly impact the sample's macroscopic properties. One solution for improving DR has been to remove the solvent from the chromatographic effluent and deposit the sample on a germanium disc (LC-transform approach). Although the mass of deposited sample is low, with current instrumentation such as DISCOVER IR from spectra analysis, sensitive techniques such as infrared spectroscopy can be used to extract chemical information with multiple scans.[37] Yet, for thermal analysis by, e.g., DSC the sensitivity has to be augmented by using the commercially available HyperDSC approach.[35] Interestingly, for the LC separation of small molecules, where typically highly sensitive detectors like mass spectrometry are used, the use of a multiple injection method has been reported.[38] However, this approach has never been applied to polymers and polyolefins in the open literature. This is surprising, as due to the heterogeneities with regard to CCD and MMD present in these materials, the question of DR is a notoriously inherent issue when it comes to LC and multidimensional LC in particular. In this study, we want to show how the amount of sample in the chromatographic effluent, and with this the DR, can be massively increased. This will open new perspectives on the detection side of 2D HT-LC, but also paves the way towards a compositional fractionation of polyolefins on a larger scale.

Table 1. Molecular characteristics of statistical E/O copolymers.

Sample code	$\overline{M}_w$ [kg mol^{-1}]	1-octene [mol%]
E/O_0	104.2	0
$E/O_{13.9}$	123.4	13.9
$E/O_{55.9}$	36.0	55.9
E/O_{100}	1.9	100

Table 2. The blend compositions.

Blend code	Weight ratio			
	E/O_0	$E/O_{13.9}$	$E/O_{55.9}$	E/O_{100}
Blend 1	0.25	0.25	0.25	0.25
Blend 2	0.33	0.33	0.33	–

2. Experimental Section

2.1. Solvents and Polymer Samples

1-Decanol and 1,2,4-trichlorobenzene (TCB) were used as received from Merck, Darmstadt, Germany. Statistical ethylene/1-octene (E/O) copolymers and their molecular characteristics (Table 1) were provided by The Dow Chemical Company, Freeport, USA. Their weight-average molar masses were determined with SEC using PE standards for the SEC calibration. These polymer samples have a dispersity of 2.0 to 2.2.

Based on the E/Os in Table 1, two blends, as shown later in Table 2, were prepared.

2.2. High-Temperature Two-Dimensional Liquid Chromatography (2D HT-LC)

A prototype chromatographic system for 2D HT-LC, constructed by PolymerChar (Valencia, Spain), was used. It consisted of an auto-sampler and two pumps equipped with vacuum degassers (Agilent, Waldbronn, Germany). Of the two ovens present, one was used to isothermally heat the SEC column, while the other one, which also houses the injector and switching valves, was used to heat the HT-SGIC column. An electronically controlled eight-port valve EC8W (VICI Valco instruments, Houston, Texas, USA) equipped with two 200 μL loops, was used to connect the HT-SGIC (first dimension) and the HT-SEC (second dimension) column. It was switched every 1 min to inject the effluent from the HT-SGIC into the HT-SEC column. A Hypercarb column, 4.6 mm × 250 mm (ID × L), packed with porous graphitic carbon particles of 5 μm diameter served as stationary phase for HT-SGIC, whereas for the second dimension a PL Rapide H column, 7.5 mm × 150 mm (ID × L), packed with poly(styrene-co-divinylbenzene) of 10 μm particle size (Agilent Technologies), was used. A flow rate of 0.2 mL min^{-1} with a linear gradient of

Table 3. Composition of the mobile phase in the gradient pump (HT-SGIC) and calculated composition of the mobile phase in the ELSD.

Desorption promoting solvent [vol%]	Linear gradient — time in pump [min]	
	Without the delay	With the delay
0	0	0
0	20	44.2
100	70	94.2
100	90	114.2
0	91	115.2

1-decanol→TCB was used in the first dimension, whereas a flow rate of 2.5 mL min^{-1} (TCB) was maintained in the second dimension. The total delay volume (defined as the system delay) of the system was calculated to be 4.84 mL according to refs. [31,33] Samples were prepared in 1-decanol at various concentrations depending on the experiment. In the HT-SGIC step, the composition of the mobile phase in the cell of the ELSD was calculated based on the delay volume of 4.84 mL (i.e., 24.2 min at a flow rate of 0.2 mL min^{-1}, Table 3). The columns were purged with 70 mL of TCB after each analysis to clean the column. The data in Table 3 enable to localize the solvent gradient in the chromatograms.

3. Results and Discussion

One classic approach in 2D HT-LC to enhance the detector response was to increase sample concentration from the commonly used 1–2 mg mL^{-1} to 4–6 mg mL^{-1}.[34] Such an increase in concentration of a polymer solution may, however, turn out to be extremely impractical for some high $\overline{M}_w$ samples as this leads to a sharp increase in viscosities, which then causes problems in the injection. The second common approach was to increase loading by using large sample loops while keeping the sample concentration constant. Blend 1 (Table 2) was analyzed by 2D HT-LC with sample loops of 200 µL and 1000 µL, respectively. Figure 1 shows the resulting color coded contour plots where the Y-axis represents the first step HT-SGIC separation and the *x*-axis the second-step HT-SEC separation (the color code represents the ELSD responses of the polymer samples). The elution volumes at peak maximum (E_{pmax}) and the corresponding signal intensities are listed in Table 4. From Figure 1 and Table 4 it can be concluded that the E/Os are separated based on their 1-octene content in the HT-SGIC step, which agrees with previous literature. E/O_{100} is partially adsorbed as can be seen in Figure 1 and the non-adsorbed part is flushed out with the adsorption promoting solvent (1-decanol). In the SEC step, the differences in the E_{pmax} are in accordance with their $\overline{M}_w$s (Table 1).

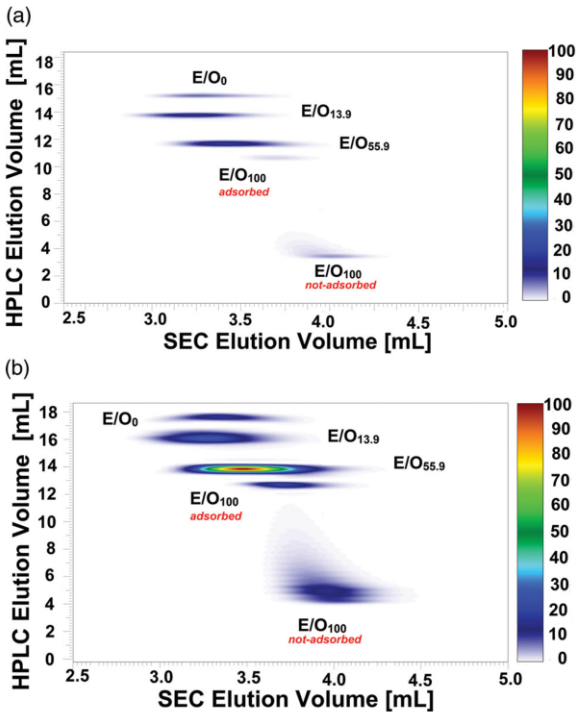

Figure 1. Contour plot from 2D HT-LC analysis of blend 1 (Table 2) with a sample loop volume of a) 200 µL and b) 1000 µL. Maximum peak intensities 1.26 V.

From Figure 1, it can be clearly seen that the larger sample loop improves the peak intensities. However, at the same time, the peaks are shifted towards higher elution volumes on their HT-SGIC axis (1.5–1.8 mL) while the SEC axis remains constant. This may be explained by the fact that the sample loading loop also forms a part of the system in the HT-SGIC step and hence the usage of a larger loop results in an increase of the delay of this system, which in turn manifests as a peak shift to larger elution volumes in HT-SGIC. As the effluent from the first step is

Table 4. E_{pmax} in HT-SGIC and HT-SEC steps for 2D HT-LC of blend 1 with 200 and 1000 µL sample injection loop.

Sample code	E_{pmax}			
	200 µL sample loop		1000 µL sample loop	
	HT-SGIC	HT-SEC	HT-SGIC	HT-SEC
E/O_0	15.19	3.24	17.02	3.23
$E/O_{13.9}$	13.77	3.19	15.55	3.22
$E/O_{55.9}$	11.66	3.42	13.39	3.40
E/O_{100} (adsorbed)	10.62	3.72	12.30	3.72
E/O_{100} (not-adsorbed)	3.39	4.05	4.89	4.02

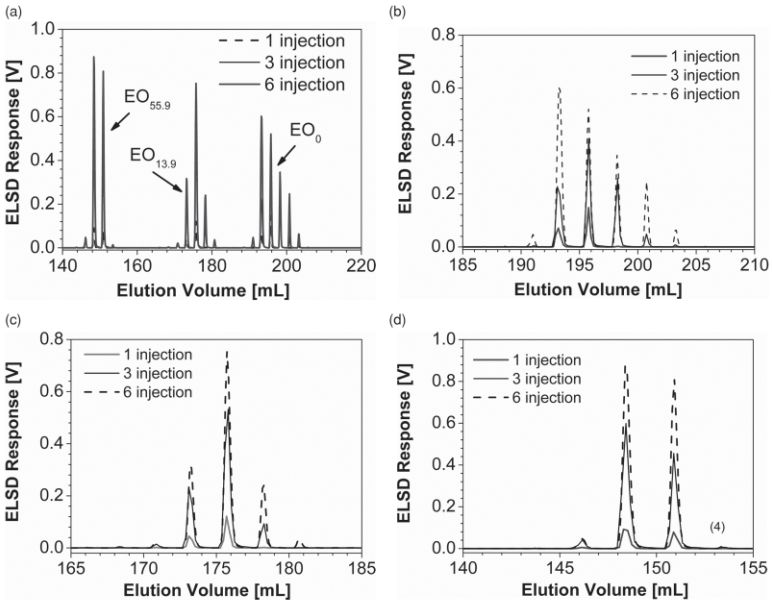

Figure 2. Overlay of chromatograms of (a) blend 2 and focused on (a) E/O_0, (b) $E/O_{13.9}$, and (c) $E/O_{55.9}$ obtained from 2D HT-LC with varying numbers of injections.

fractionated and then fed into the current HT-SEC set-up, the delay caused by a larger sample loop does influence the SEC separations. For gradient LC separations, elution volumes are regularly used to identify various macromolecule species (e.g., allocate an eluting fraction to a comonomer content) so this additional shift on the HT-SGIC axis would be detrimental to the interpretation of the results from the 2D HT-LC experiment. It is therefore critical that the calibration of the HT-SGIC dimension is performed with the same experimental setup. The E_{pmax} for different sample loops were calculated on basis of their system delay and compared with experimental data. The experimental E_{pmax} were larger than the calculated values due to the differences in diffusion along the chromatographic systems. A more severe problem experienced upon using larger sample loops was the irreproducibility of injections. Owing to larger volume of a viscous sample solution, the injector syringe was unable to precisely inject the programmed amount of the larger sample plug in the 1000 mL loop. This experimental limitation manifested in the form of non-reproducible injections. Because of the above reason, larger sample loops may not be used as a reliable tool for 2D HT-LC where the E_{pmax} plays a determining role in identification of various polymer components.

To minimize the above-mentioned problems, the desired scenario would be to use the same sample loop for injection, which gives best reproducibility of injections in the 2D HT-LC setup (which here is the 200 µL sample loop). To achieve better DR, an alternative is proposed. It uses an approach of multiple injections, which has been reported earlier for reversed-phase HPLC, to achieve preparative LC separations.[38] This method has only been reported for small molecule separations and can be used in a slightly modified form for synthetic polymers, for the first time, to solve the problems discussed above. In this approach, multiple portions of the same sample solution are injected onto the stationary phase before desorption is started. Separate testing of the sample capacity with a Hypercarb 100 mm × 4.6 mm column revealed that as much as 30 mg of PE 55 kg mol^{-1} could be adsorbed. A particularly attractive feature of this procedure is that the delay, which would be introduced by increasing the sample loop as well as the increased viscosity when using more concentrated sample solutions can both be avoided. To probe the feasibility of this approach for 2D HT-LC, a solution of a model blend was repeatedly injected into a Hypercarb column flushed with the adsorption promoting solvent (1-decanol) using a 200 µL sample loop prior to starting the desorbing step. Thereafter, desorption was started by applying a linear solvent gradient of 1-decanol→TCB. Figure 2 shows the SEC traces from the 2D HT-LC analysis for varying numbers of injection. As may be seen the DRs of the fractionated peaks increased as number of injections is increased.

Table 5. The E_{pmax} in HT-SGIC and HT-SEC derived from 2D HT-LC contour plot of blend 1 for different number of injections.

No. of injections	1		3		6	
Sample code	E_{pmax} [mL]					
	HT-SGIC	HT-SEC	HT-SGIC	HT-SEC	HT-SGIC	HT-SEC
E/O_0	15.34	3.22	15.36	3.24	15.35	3.24
$E/O_{13.9}$	13.75	3.17	13.76	3.19	13.77	3.18
$E/O_{55.9}$	11.62	3.37	11.65	3.38	11.66	3.38

The corresponding color-coded contour plots of the 2D HT-LC analysis are shown in Figure 3. From Table 5 the E_{pmax} obtained from the contour plots (Figure 3) can be also seen to be almost unchanged.

To illustrate this improvement, the cumulative peak areas of the SEC-traces for each component of blend 2 from Figure 2 are plotted as a function of the number of injections in Figure 4.

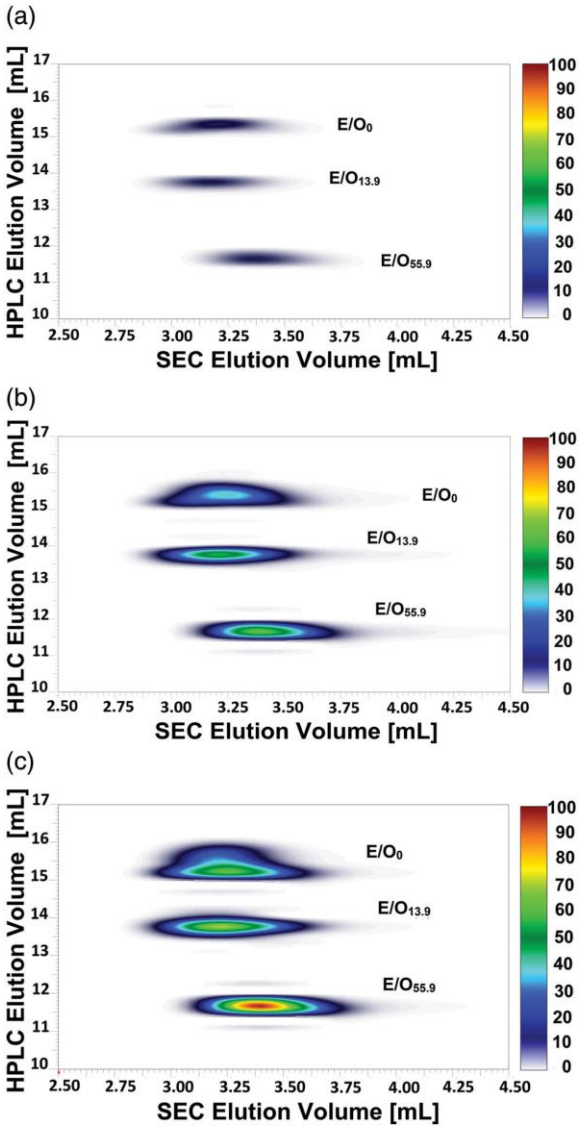

Figure 3. Contour plot from 2D HT-LC analysis of blend 2 injected a) 1 times b) 3 times and c) 6 times; Maximum intensity of the ELSD response is 1.05 V (100% in the color scale).

The peak areas increase with the number of injections, however, the slope in Figure 4 is found to be non-linear. This is due to the fact that the response of the ELS-detector used here is determined by concentration of the polymer (in this case 1-octene content), however, the response may also be a function of the composition of the mobile phase, composition of polymer and the polymer's molar mass. An extensive review on this is given in ref.[39] Although the influence of the mobile phase on the detector signal should be subordinate as the elution occur isocratic, the systematic difference in signal increase for the individual

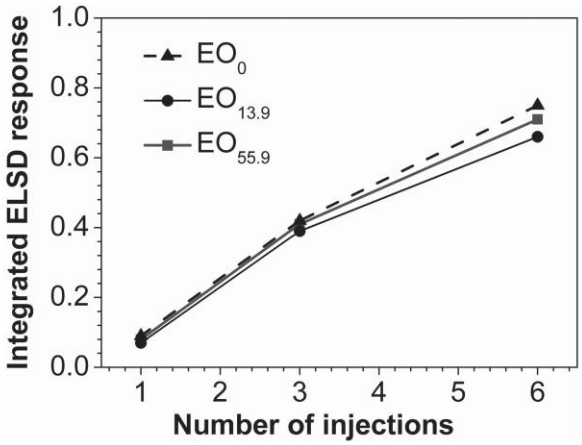

Figure 4. Integrated ELSD response from Figure 2 of blend 2 separated with 2D HT-LC, plotted against the number of injections.

blend components may be explained by their different average molar mass and chemical composition. It should be mentioned that the response of other detectors like RI and IR may also depend on a sample's composition, albeit to a smaller extent. However, IR and RI cannot be used in SGIC as the used mobile phase is also detected. On the other hand, ELSD is applicable for the gradient elution and moreover, it offers often higher responses for polyolefins, than RI or IR detector.

Clearly, the approach of multiple injection and sample accumulation on the stationary phase leads to a significant enhancement in information from 2D HT-LC by amplifying the DR. Yet, an enormous potential of this technique becomes obvious when considering the hyphenation of 2D HT-LC (or HT-LC) systems with post separation characterization. A direct benefit lies in the on-line hyphenation, e.g., with NMR in on-flow mode,[40–42] where solvent signal suppression by special pulse sequences is required. But in the same sense an improved amount of analyte is helpful for off-line characterization by for example DSC, where the now standard DSC instrumentation and methods may then be used instead of HyperDSC and thus quantitative data can be obtained.

4. Conclusion

Poor detector response is often a hindrance in the interpretation of 2D HT-LC separations. Using higher sample concentrations or increasing the sample loops have the drawback of increased viscosities and shifts in elution volume, respectively, and are therefore not an appropriate solution. In this study, we demonstrated for the first time for polymers that multiple injections of a sample and then starting the desorption step avoids these drawbacks.

Within the scope studied here, no change in the elution volume at peak maxima could be observed and no overloading of the stationary phase occurred.

Acknowledgements: This research forms part of the research collaboration between Group of Material Analytics, Fraunhofer Institute, LBF, Darmstadt and Dow Chem. Co., USA. The authors also thank Dr. A. Ginzburg for his valuable advice.

Received: October 10, 2013; Revised: November 11, 2013; Published online: January 16, 2014; DOI: 10.1002/macp.201300649

Keywords: carbon sorbents; detector response; graphite; polyolefins; two-dimensional liquid chromatography

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6.3 HT-LCCC of polyethylene

HT-HPLC has been an important analytical tool for unravelling the molecular heterogeneities of polyolefins. Depending on the mechanism of separation, HT-HPLC can be sub-divided into the modes of HT-SEC, HT-LAC and HT-LCCC. HT-SEC-based separations are entropy-controlled and have been routinely applied to determine the MWD. HT-LAC has been developed recently as a result of the finding that polyolefins can be reversibly adsorbed from solution on graphite, and has since then found application to determine the CCD of polyolefins[73-77]. HT-LCCC as a separation mode exists at the borderline between HT-SEC and HT-LAC where the entropic term and the enthalpy change precisely compensate each other. At these conditions the chains of a given repeating unit may be separated based on differences in their microstructure or composition, independent of their MW (Figure 1 a).

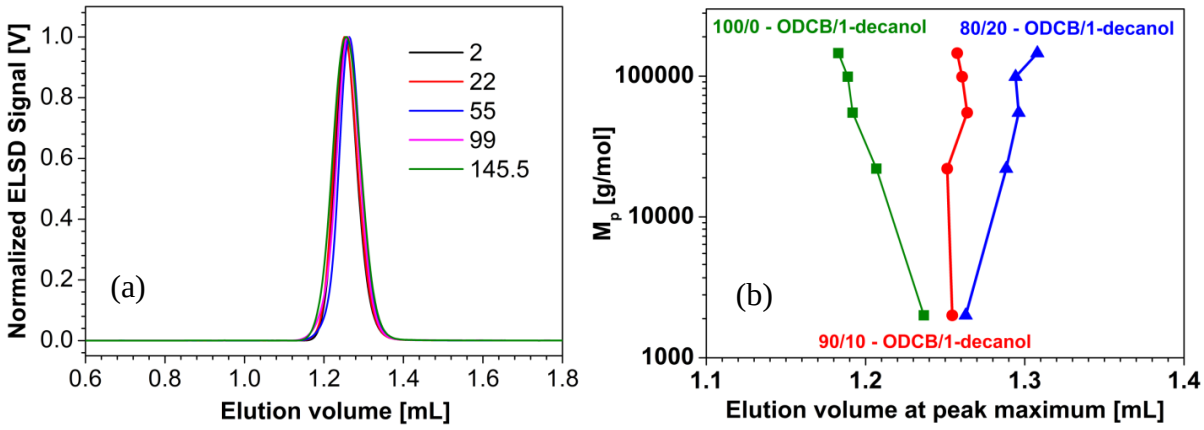

Figure 1: a) Overlay of chromatograms of HDPE standards at critical conditions for the system Hypercarb™, 1-decanol/1,2-dichlorobenzene (ODCB), at 160 °C. and the corresponding b) MW versus elution volume at peak maximum plot showing all three chromatographic modes.

In this work, for the first time, HT-LCCC of linear PE using PGC (Hypercarb™) as stationary phase in various mobile phases at 160 °C will be presented (Figure 1 b). As an application example HT-LCCC was applied to separate E/O statistical copolymers with similar MW.

Polymer 54 (2013) 5518–5524

Contents lists available at ScienceDirect

Polymer

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Liquid chromatography at critical conditions of polyethylene

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ARTICLE INFO

Article history:
Received 1 July 2013
Received in revised form
15 August 2013
Accepted 16 August 2013
Available online 24 August 2013

Keywords:
Liquid chromatography at critical conditions
Polyethylene
Porous graphitic carbon

ABSTRACT

Olefin copolymers are of increasing scientific interest due to their important application potential. Liquid chromatography can deliver important information, especially on their molecular structure. In particular, liquid chromatography at critical conditions (LCCC) is of interest because, in this chromatographic mode, the elution is molar mass independent for a given repeat unit. LCCC is conducted at conditions where the entropic effect of size exclusion is equal to the enthalpic effect of interaction between the macromolecules and the stationary phase and can be used to separate copolymers as well as some homopolymers containing one single repeat unit but having different end groups. For the first time, critical conditions for linear PE were experimentally identified by using porous graphite (Hypercarb™) as the stationary phase, and either 1-decanol/ortho-dichlorobenzene (ODCB), 1-decanol/1,2,4-trichlorobenzene (TCB), *n*-decane/ODCB, or *n*-decane/TCB as the mobile phase at 160 °C. The identified critical conditions for PE using the above approach in the above solvents have been verified to be correct, barring slight deviations, by two different techniques which were previously used to determine critical conditions for polymers soluble at ambient temperature. The critical conditions for polyethylene were applied to separate statistical copolymers of ethylene/1-octene with similar molar mass.

1. Introduction

Liquid chromatography (LC) may provide valuable insight into the various distributions of molecular parameters present in a polymer sample. In the study of chain heterogeneity of polymers, the most important ones are the molar mass distribution (MMD) and the chemical composition distribution (CCD). Size Exclusion Chromatography (SEC) is routinely used to determine the MMD and Liquid Adsorption Chromatography (LAC) provides a tool to characterize the CCD. SEC is an entropy controlled process where the macromolecules are separated according to their hydrodynamic volume, i.e., the extent to which they are excluded from a porous stationary phase. LAC on the other hand is enthalpy controlled and the macromolecules are separated as a result of their physicochemical interaction with a stationary phase. Consequently, the elution behaviour of macromolecules in SEC and LAC is different. While in SEC the large polymer chains elute first, the opposite is the case in LAC. At the borderline between SEC and LAC a point exists where entropic and enthalpic interactions precisely compensate for each other. At these conditions, referred to as critical conditions, macromolecules, containing identical repeat units, elute independently of their molar masses, and their elution behaviour is determined by subtle structural differences. The existence of LCCC was first theoretically proven by Benlenkii et al. [1], Entelis et al. [2], and Skvortsov [3]. Since then, this chromatographic modus has been experimentally applied for a series of separations [4–14] for polymers which are soluble at room temperature. More than 150 LCCC systems were known up to 2003 [15], that have been used to separate copolymers [11,15], as well to separate homopolymers (identical repeat unit) that solely differ in their end groups [2,11,15–18].

Segmented copolymers of olefinic monomers are of increasing scientific interest, as they elegantly allow combining the macroscopic properties of different homopolymers, which are physically not miscible. Progress in catalyst technology, e.g., the chain shuttling approach, has recently enabled the large scale production of ethylene/1-octene (E/O) copolymers [19]. To establish structure ↔ property relationships and to rationally improve catalyst selectivity for this class of materials, an in depth analysis of their molecular structure is indispensable [19]. In particular the

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http://dx.doi.org/10.1016/j.polymer.2013.08.040

the Hypercarb™ column which was kept at 160 °C. A mixture of two solvents that differ in their solvation strength was used as the isocratic mobile phase for PE. To determine conditions for LCCC, an interactive mode is needed in addition to size exclusion mode. To fulfil this criterion four solvents which have been traditionally used for interaction based PE separations were selected. Two of these are weak eluents, i.e., 1-decanol and *n*-decane, which promote the adsorption of PE on the column packing, while the remaining two are strong eluents, i.e., TCB and ODCB, enable desorption of PE [25–30]. By varying the ratio of weak to strong eluent the overall elution strength of the isocratic mobile phase is modified accordingly. Using this approach of systematically changing solvent strength, the elution behaviour of PE was measured in neat TCB and ODCB as well as in their binary mixtures with 1-decanol and *n*-decane. Representative chromatograms are shown in Figs. 1 and 2.

PE standards elute in TCB and ODCB in size exclusion mode covering a narrow range of the retention volume. The hydrodynamic dimensions of the PE standards in TCB and ODCB may slightly differ, but this alone cannot explain the significant discrepancy in the elution volume of corresponding samples in TCB and ODCB (Fig. 1b). The molar mass dependency of the retention volumes of PE clearly implies exclusion mode (Fig. 1a and b), however, both the higher elution volume of PE in ODCB and tailing (deformation) of the PE peaks (Fig. 1b), indicate enthalpic interactions with the stationary phase. With the addition of a weak eluent (1-decanol or *n*-decane) to TCB or ODCB, the elution volume of PE increases (Fig. 2) due to increasing interaction of the macromolecules with the graphitic surface. When the concentration of weak solvent is further increased, at a certain solvent mixture composition, all standards are equally retained and elute at the same volume. This composition was identified as the critical composition of the particular solvent mixture for PE at the stated temperature (Fig. 3). The elution volume at peak maximum, Ep_{max}, is plotted against the average molar mass of PE standards' for TCB/*n*-decane and ODCB/1-decanol as shown in Figs. 4 and 5. At 160 °C the critical conditions for PE in ODCB/1-decanol are reached at 90/10 vol. %, and for TCB/*n*-decane at 48.5/51.5 vol. % (Fig. 3). Noteworthy from Fig. 5 is that a critical condition for TCB/*n*-decane exists between 48/52 vol. % and 48.5/51.5 vol. %. The balance between the modes of SEC and LAC is very sensitive in this region and the transition occurs rapidly, so only a range can be defined for this particular solvent combination. However for all practical purposes either of 48/52 or 48.5/51.5 vol. % may be taken as value and the latter has been taken as the critical condition here for this particular chromatographic system. M_p is plotted as a function of Ep_{max} for the above four solvent mixtures in Figs. 4–7 and the results are summarized in Table 3.

Sample recovery problems, which are commonly associated with LCCC for high molar mass samples, were not observed in these experiments. It should also be noted that the relatively poor SEC calibration curves shown in Figs. 4–7 may be due to the low column dead volume of the Hypercarb™ column and may be improved by using columns with larger dimensions or different porosity. While PE has been known to adsorb from thermodynamically poor solvents (e.g. 1-decanol) [37], adsorption of PE from *n*-decane, which is a thermodynamically good solvent, is an interesting phenomenon [38,39]. This may be explained by considering the increase of adsorption energy with the increase in molar mass of polymers [37]. Hence, *n*-decane adsorbed on the graphite surface is displaced by PE being a larger molar mass homologue of *n*-alkanes.

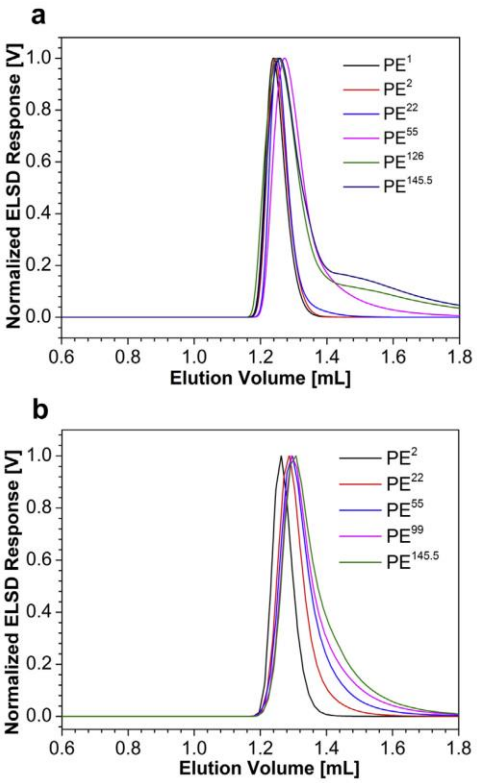

Fig. 2. Chromatograms for linear PE standards in a) TCB/*n*-decane, 48/52 vol. %; b) ODCB/1-decanol, 80/20 vol. %.

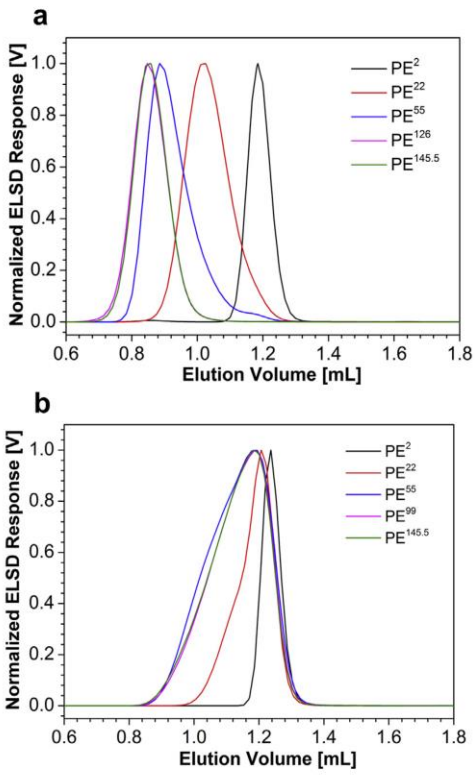

Fig. 1. Chromatograms for linear PE standards in a) TCB; b) ODCB.

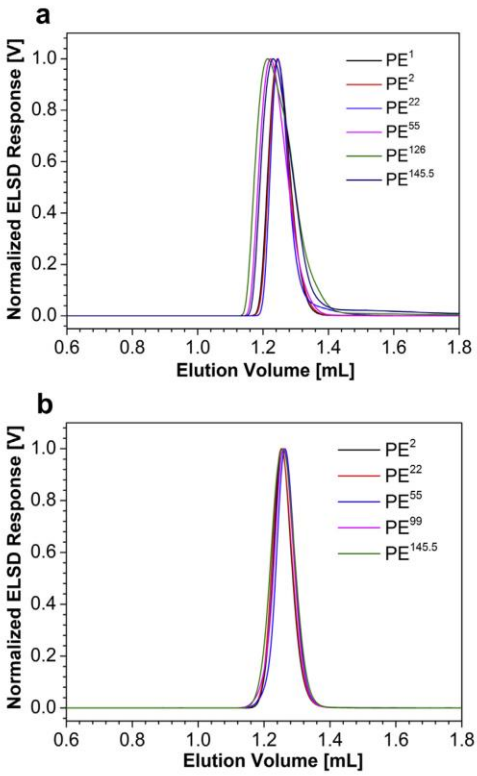

Fig. 3. Chromatogram for linear PE standards in a) TCB/*n*-decane, 48.5/51.5 vol. %; b) ODCB/1-decanol, 90/10 vol. %.

3.2. Verification of LCCC with two other methods

To confirm the critical conditions of PE determined from the above method, two alternative approaches are applied. The first one is according to Brun et al. [40,41] who hypothesized that a homopolymer of high molar mass would elute in a solvent gradient at the composition which corresponds to the critical condition of the polymer in this mixed mobile phase. This hypothesis was experimentally demonstrated by Bashir et al. [42] for the case of poly (methyl methacrylate) using silica gel as a stationary phase in a solvent gradient HPLC at room temperature. The critical solvent composition for linear PE is analogously determined according to Ref. [42] by using PE of M_p = 145.5 kg/mol and a 10 min linear gradient from weak to strong eluent. The critical solvent composition for PE on Hypercarb™ in *n*-decane/TCB and other systems was determined considering the values of both the dead and the delay volumes (Fig. 8).

The composition at Ep_{max}, namely 49.2/50.2 vol. % TCB/*n*-decane, is determined as the critical condition at 160 °C for PE. Critical conditions for PE in ODCB/*n*-decane, TCB/1-decanol and ODCB/1-decanol are determined in the same way and the results are tabulated in Table 3.

The second method was reported by Cools et al. [43] according to which the critical conditions can be determined from the crossing point of curves plotted between polymer retention and the percentage of non-solvent. This is illustrated for the example of TCB/*n*-decane in Fig. 9. For this experiment PE standards are injected into an isocratic mobile phase TCB/*n*-decane of varying composition. The weak component, i.e., *n*-decane, is the non-solvent in Fig. 9 whereas the strong solvent, i.e., TCB, is the solvent. The peak retention volumes at different volume ratios of non-solvent/solvent all converge at a non-solvent, i.e., an *n*-decane percentage, of 52. Thus 52/48 vol. % *n*-decane/TCB is the critical condition for PE determined according to Ref. [43]. The critical conditions for PE in the remaining solvent mixtures are also determined and tabulated in Table 3.

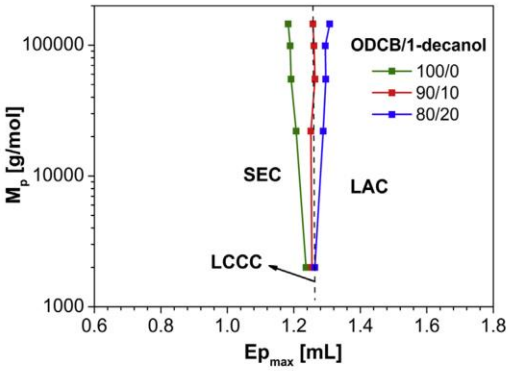

Fig. 5. Dependence between the M_p of linear PE standards and their Ep_{max} for different volume ratios of ODCB/1-decanol.

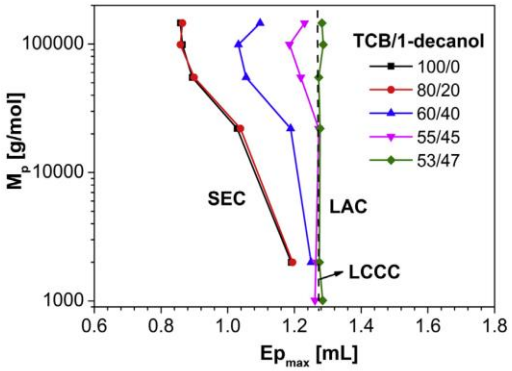

Fig. 4. Dependence between the M_p of linear PE standards and the respective Ep_{max} for different volume ratios TCB/1-decanol.

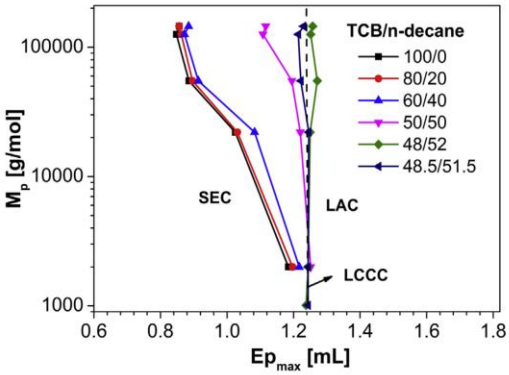

Fig. 6. Dependence between the M_p of linear PE standards and their Ep_{max} for different volume ratios of TCB/*n*-decane.

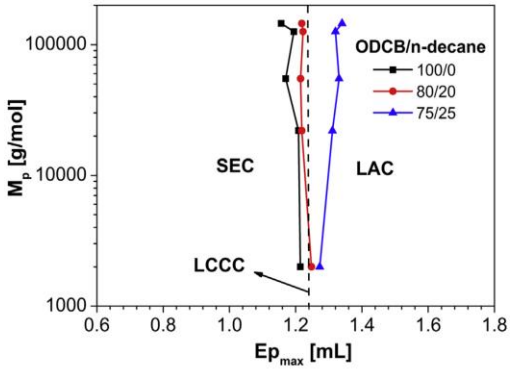

Fig. 7. Dependence between the M_p of linear PE standards and their Ep_{max} at different ratios of ODCB/*n*-decane.

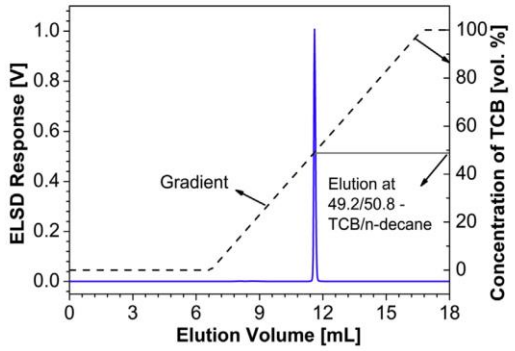

Fig. 8. Chromatogram of linear PE (M_p = 145.5 kg/mol) used to determine the critical composition according to Ref. [42]. Eluent: *n*-decane → ODCB, 10 min linear gradient.

The critical compositions determined by the three methods in Table 1 are similar within experimental errors. Noteworthy is that all three methods described above are based on indirect correlations hence the accuracy and precision of all three methods are not ideal due to experimental limitations. It is known that the elution of polymers at critical conditions may be extremely sensitive towards minute changes in eluent composition and temperature [11,15,44] Despite great care with regard to control the temperature, such small variations may be responsible for some scattering of points observed while measuring critical conditions.

Nevertheless, for all practical purposes, these results can be taken as the critical conditions of PE at 160 °C. The data in Table 3 show that a weaker eluent (1-decanol and/or *n*-decane) is needed for the TCB system to reach critical conditions at 160 °C if compared with the equivalent ODCB system. This indicates that TCB is a stronger eluent than ODCB, i.e., less TCB is needed to desorb PE compared to ODCB. Analogously, a lower concentration of 1-decanol compared to *n*-decane is needed to reach critical conditions (Table 3), confirming that 1-decanol is a weaker eluent compared to *n*-decane.

3.3. Application of LCCC of PE to separate E/O statistical copolymers

Statistical E/O copolymers with a 1-octene content of 0–13.9 mol % (Table 2) were supplied by the Dow Chemical Company. Their elution behaviour was investigated at critical conditions for PE. When overlaying the chromatograms in pure TCB (SEC mode) they all elute together (Fig. 10a) which may be expected due to their similar MMD. At critical conditions of PE, however, they elute according to their average content of 1-octene (Fig. 10b). The Ep_{max} decreases as the average 1-octene content increases, and reaches a minimum value of 0.85 mL (Fig. 10c).

The trend observed in Fig. 10 indicates that the incorporation of 1-octene influences the retention. However, this effect can only be observed if the average molar mass (and dispersity) of the copolymers are similar (Fig. 11). In the case of dissimilar MMD the above trend is less obvious (Fig. 11).)

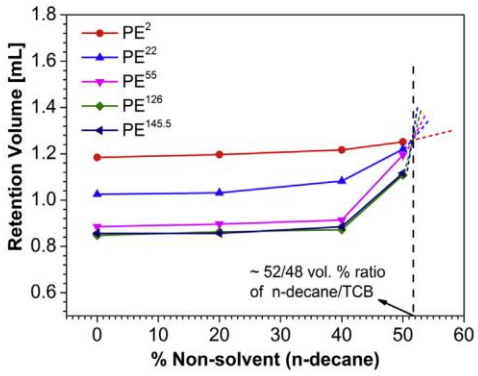

Fig. 9. Retention volume versus percentage non-solvent to determine the critical conditions of linear PE according to Ref. [43].

4. Conclusion

Critical conditions for polyethylene were for the first time identified by using linear PE standards at 160 °C. With porous graphite (Hypercarb™) as the stationary phase, four possible combinations of strong/weak solvent pairs which are commonly used in solvent gradient LAC of PE were studied. The critical conditions are 53/47, 90/10, 48.5/51.5 and 75/25 vol. %, in TCB/1-decanol, ODCB/1-decanol, TCB/*n*-decane, and ODCB/*n*-decane, respectively. These results were verified by the methods of Bashir et al. and Cools et al., which were previously used to find critical

Table 3
Composition of the mobile phase at critical conditions of PE determined via the three methods.

Solvent strong solvent/weak solvent	Critical composition of the mobile phase		
	Solvent ratio from the plots of SEC-LAC [vol. %]	Solvent ratio according to Bashir et al. [42] [vol. %]	Solvent ratio according to Cools et al. [43] [vol. %]
TCB/1-decanol	53/47	54.3/45.7	53.5/46.5
ODCB/1-decanol	90/10	87/13	88/12
TCB/*n*-decane	48.5/51.5	49.2/50.8	48/52
ODCB/*n*-decane	80/20	81.7/18.3	79.5/20.5

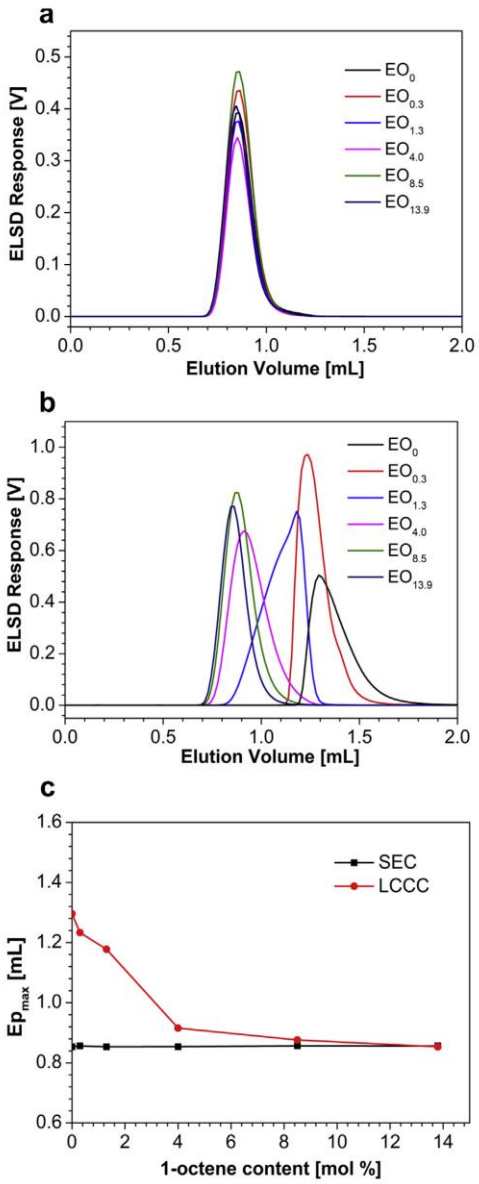

Fig. 10. (a, b and c) Overlay of chromatograms for E/O statistical copolymers. Mobile phase: a) TCB, b) TCB/*n*-decane, 48.5/51.5 vol. %. c) Corresponding plot for the Ep_{max} versus 1-octene content.

conditions for polymers soluble at room temperature. The ratios of weak/strong solvent found to achieve the corresponding critical conditions also provide a qualitative comparison relative to the adsorbing or desorbing strength of the chromatographic solvents. TCB was found to be a stronger eluent than ODCB, for PE, whereas 1-decanol was found to be a weaker eluent compared to *n*-decane, for PE. Using the thus identified critical conditions, statistical ethylene/1-octene copolymers of similar average molar mass were separated according to their content of 1-octene. In the case of dissimilar molar mass, the separation was additionally influenced by the molar mass. The critical conditions of PE which now can be determined experimentally for different solvent systems provide the perspective to determine the length of non-ethylene blocks in

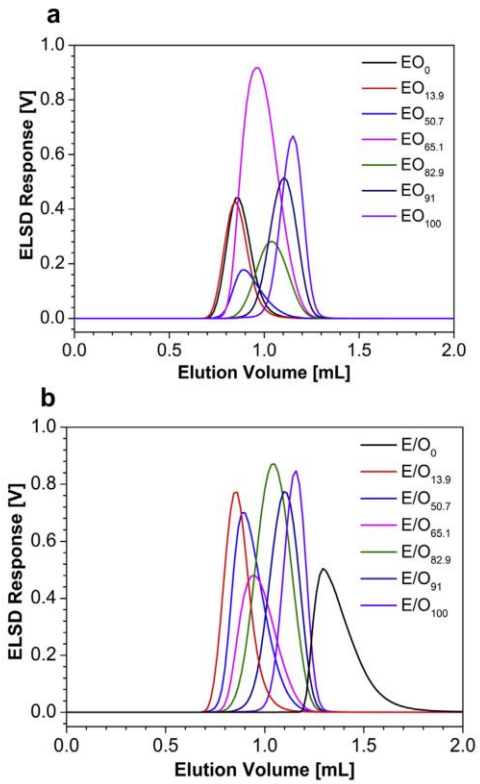

Fig. 11. Overlay of chromatograms for E/O statistical copolymers (composition of the copolymers in mol. % of 1-octene is indicated in the figure). Mobile phase: a) TCB, b) TCB/*n*-decane, 48.5/51.5 vol. %.

di- and tri-block copolymers containing polyethylene blocks. This information may crucially complement results from NMR which is widely used to determine short range monomer sequences in polymers.

Acknowledgement

This research forms part of the research collaboration between Material Analytics Group, Fraunhofer Institute, LBF, Darmstadt and the Dow Chemical Company, USA. The authors acknowledge the fruitful discussions with Dr. M. Miller, Dr. W. Winniford, Dr. J. Lyons and Dr. D. Lee from the Dow Chemical Company.

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6.4 Application of binary solvent mixtures in HT-TGIC

HT-TGIC is an emerging analytical tool to determine the CCD of polyolefins[90,91]. An advantage is the fact that HT-TGIC enables separation of copolymers in a larger comonomer range compared to crystallization based techniques like CEF. However, in the case of ethylene/α-olefin copolymers the chromatographic resolution of HT-TGIC is significantly lower than that of CEF[44]. ODCB and TCB have until recently been the preferred mobile phase in HT-TGIC. This research aims at improving the resolution in HT-TGIC by varying the composition of the mobile phase and making use of the knowledge of conditions for HT-LCCC.

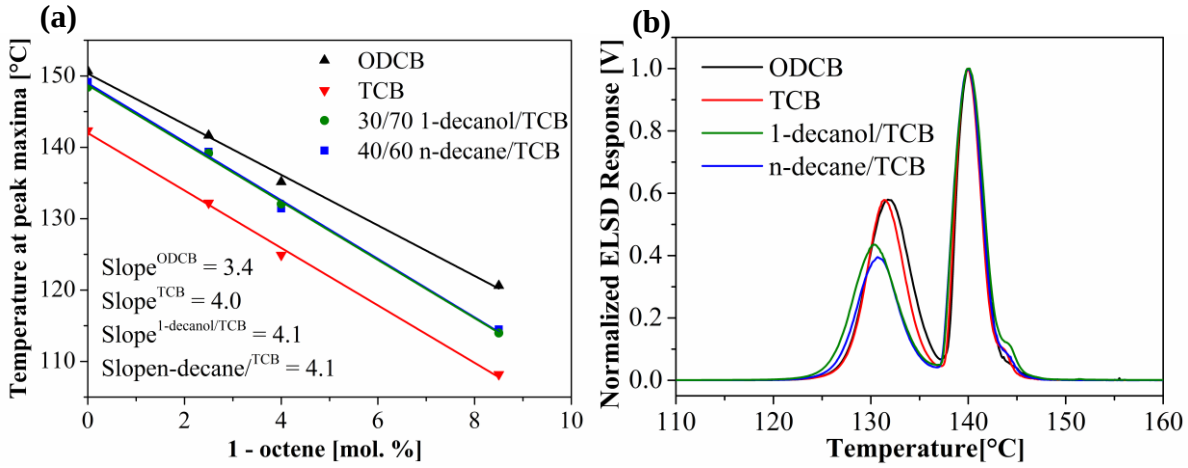

Figure 1: HT-TGIC based (a) Temperature versus 1-octene content plot and (b) Overlay of chromatograms corresponding to 1:1 model blend of E/O copolymers containing 0.3 and 2.5 mol. % 1-octene. Peaks are normalized based on the peak intensity of E/O 0.3 mol. %, and elution volume was shifted to 140 °C to overlay. Note: Stationary phase is PGC (Hypercarb™). Mobile phases are ODCB, TCB, 30/70 (v/v) 1-decanol/TCB, and 40/60 (v/v) n-decane/TCB.

Building on the method development for HT-LCCC binary solvent systems were applied as mobile phase for the separation of E/O statistical copolymers. By comparing the resolution from the above experiments and by using theoretical calculations optimized solvent systems were determined. These optimized systems were then applied as mobile phase for HT-TGIC to separate a model blend of two E/O statistical copolymers giving evidence of the industrial applicability.

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Studying Binary Solvent Mixtures as Mobile Phase for Thermal Gradient Interactive Chromatography (TGIC) of Poly(ethylene-*stat*-1-octene)

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ABSTRACT: Thermal gradient interactive chromatography (TGIC) is an emerging analytical tool to determine the chemical composition distribution of polyolefins. TGIC separates polyolefins based on their interaction with graphitic carbon at different temperatures in an isocratic mobile phase. In the case of copolymers of ethylene and 1-olefins, TGIC offers a larger commoner range of separation than crystallization based techniques. However, currently TGIC shows approximately only half of the resolution compared to crystallization based techniques for an ethylene content higher than 92 mol % when 1,2-dichlorobenzene (ODCB) and 1,2,4-trichlorobenzene (TCB) are used as the mobile phase. We conducted a systematic study exploring the potential of using different binary solvent mixtures as the mobile phase to increase the resolution in TGIC of poly(ethylene-*stat*-1-octene). Apart from the well-established chlorinated aromatic solvents like ODCB and TCB, for the first time, binary solvent mixtures containing alkanes and aliphatic alcohols have been evaluated as components of the mobile phase using an evaporative light scattering detector. As an outcome, optimized binary solvent mixtures could be identified that enabled an improvement in resolution. This was exemplarily verified by separating a model blend of two poly(ethylene-*stat*-octene) samples with varying 1-octene content.

■ INTRODUCTION

Polyolefins are, by volume, the most important synthetic polymers with an annual production expected to reach 200 million metric tons by the year 2020.[1] Due to their extremely versatile end-use properties paired with a good cost/performance ratio, polyolefins are being accepted in many novel and diverse applications. This versatility arises from the ability to control molecular heterogeneities by advances in catalyst[2,3] and process technology.[4] At the same time, this creates the need to develop accurate and more comprehensive analytical techniques for molecular characterization. The molecular heterogeneities in polyolefins can be defined, to a large extent, by the average molecular weight (MW) and the underlying molecular weight distribution (MWD), the chemical composition (CC), and the distribution with regard to composition (CCD). MW and MWD are determined routinely by high temperature size exclusion chromatography (HT-SEC, or SEC), which separates the macromolecules according to differences in their hydrodynamic volume leading to preferential exclusion from a porous noninteracting stationary phase.[5] The CC of polyolefins is routinely determined by thermal analysis[6−8] and spectroscopic techniques such as Fourier transform infrared spectroscopy (FTIR)[9,10] and nuclear magnetic resonance (NMR).[11,12] The CCD of polyolefins has for a long time been determined by crystallization based techniques like temperature rising elution fractionation (TREF),[13] crystallization analysis fractionation (CRYSTAF)[14] and, more recently, crystallization elution fractionation (CEF).[15] All of them are based on the crystallizability of macromolecules from a dilute solution, which is a function of composition, and hence cannot be used in the case of amorphous materials. Additionally, cocrystallization may complicate the interpretation of the results obtained from crystallization based techniques.[16] Recently, high temperature liquid adsorption chromatography (HT-LAC or LAC) using porous graphitic carbon (PGC) as the stationary phase has emerged as an alternative to determine the CCD of polyolefins.[17−20] LAC separates macromolecules based on their selective adsorption onto a graphitic surface at a specific temperature and composition of the mobile phase. The selective adsorption can be realized by keeping the temperature constant and varying the strength of the mobile phase (solvent gradient interactive chromatography, SGIC),[17−23] or by keeping the mobile phase composition constant and varying the temperature (thermal gradient interactive chromatography, TGIC).[24−27] Both techniques, however, enable the separation of polyolefins in a broader comonomer range compared to TREF, CEF, and CRYSTAF. SGIC facilitates separation of olefin copolymers over the full range of comonomer content,[28] whereas TGIC enables a larger choice of detectors.[24]

TGIC based separations were first demonstrated by Lochmüller[29] and Chang[30−32] for polyethylene glycol and

Received: June 16, 2014
Revised: September 1, 2014
Accepted: September 9, 2014
Published: September 9, 2014

dx.doi.org/10.1021/ie502423h | *Ind. Eng. Chem. Res.* 2014, 53, 15183−15191

polystyrene, which are soluble at room temperature. Until recently, the lack of knowledge about conditions for LAC hindered the application of the concept of TGIC to polyolefins. This was overcome with the use of graphite as the stationary phase[17−20] and subsequently, Cong et al. reported TGIC of polyolefins where they separated HDPE, PP of varying tacticity, and poly(ethylene-*stat*-1-octene) (E/O) using a column packed with PGC in 1,2-dichlorobenzene (ODCB) and 1,2,4-trichlorobenzene (TCB) as mobile phases.[24−27] TGIC enables one to separate E/O over a larger comonomer range, compared to TREF, CEF, and CRYSTAF, but is limited in terms of separation resolution when the ethylene content is >92 mol %.[26,33,34] Hence, numerous studies have been conducted to further improve the resolution of TGIC separations. Soares et al. evaluated the influence of sample concentration, cooling rate, cooling flow rate, heating rate and range of the temperature gradient on the resolution with PGC as stationary phase.[27,35] Various alternative substrates, such as boron nitride and molybdenum- and tungsten sulfide have been evaluated with regard to their potential as stationary phases for TGIC of E/O, but the results were comparable to those with PGC.[36,37] For TGIC of polyolefins, the preferred mobile phases[24−27,37] have been ODCB and TCB. Phenol[37] and 1-chloronaphthalene[38] are other solvents that were tested as alternatives, however, without much improvement in the resolution. In this paper, a comprehensive study will be conducted on the application of a variety of solvents differing in their solvation and adsorption promoting quality as the mobile phase for separating E/O by TGIC. The potential of using binary mobile phases will be explored and the influence of the mobile phase composition on the resolution in TGIC of E/O will be investigated. In this study, an evaporative light scattering detector will be employed to enable the application of alkanes and alcohols as components of binary solvents for TGIC, in addition to ODCB and TCB, which have been commonly used as mobile phases. On the basis of the calculated chromatographic resolution, optimized mobile phase compositions will be identified, which then will be applied to separate a model blend of E/O under standard TGIC conditions as proof of concept.

EXPERIMENTAL SECTION

1,2-Dichlorobenzene (ODCB), 1,2,4-trichlorobenzene (TCB), 1-decanol, *n*-decane, and diphenyl ether (DPE) were used as received from Merck, Darmstadt, Germany. These solvents were used to dissolve the polymer samples as well as the mobile phases in TGIC. The cloud point temperatures of high density polyethylene (PE, M_W = 260 kg/mol, $Đ$ = 3−5, PCD, Linz, Austria) in these solvents, determined by Macko et al.,[39] are listed in Table 1. In general, solvents with lower cloud point temperatures are thermodynamically better solvents for PE.

Table 1. Cloud Point Temperature Measured as in Ref 39

solvent	cloud point temperature (°C)
ODCB	87
TCB	88
n-decane	90.8
1-decanol	138
DPE	152.5

E/O in (Table 2) were synthesized and characterized by The Dow Chemical Company, Freeport, USA. The dispersity of all materials was around 2.2.

Table 2. List of E/O Samples

sample code	M_W (kg/mol)	1-octene (mol %)
E/O_0	104.2	0
$E/O_{0.3}$	105.9	0.3
$E/O_{2.5}$	103.8	2.5
$E/O_{4.0}$	102.9	4
$E/O_{8.5}$	111.2	8.5
$E/O_{13.9}$	123.4	13.9

The polymer solutions with a concentration of ∼1 mg/mL were prepared by dissolving the samples in the respective mobile phase at 160 °C for 2 to 3 h.

The TGIC measurements were performed on a commercially available instrument from Polymer Char, Valencia, Spain. The equipment incorporated the automated sample preparation with integrated filtration. An injection loop of 200 μL was used. The temperature program shown in Figure 1 was applied with a cooling rate, cooling flow rate, heating rate, elution flow rate of 3 °C/min, 0.02 mL/min, 2.5 °C/min, and 0.5 mL/min, respectively, for all experiments.

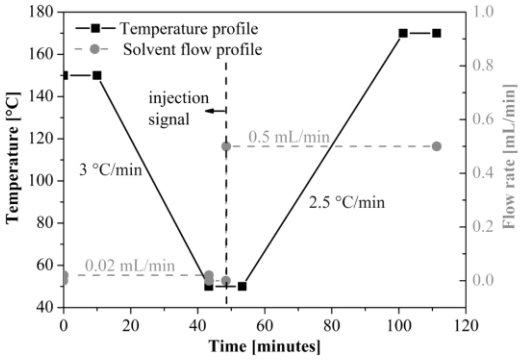

Figure 1. Profiles of temperature and flow rate applied for all the TGIC experiments.

An evaporative light scattering detector (ELSD), model PL-ELS 1000 (Polymer Laboratories, Church Stretton, England), was used to monitor the composition of the effluent. The nebulizer temperature and the evaporation temperature were fixed at 170 and 260 °C, respectively, with a nitrogen flow rate of 1.5 L/min. Data collection (1 point/s) and processing were done using WinGPC software from Polymer Standards Services, Mainz, Germany.

A Hypercarb column, 4.6 × 100 (mm) IDxL (Thermo Fisher Scientific, Dreieich, Germany), packed with spherical particles of porous graphitic carbon with a diameter of 5 μm, was used for all experiments in this paper.

The reproducibility of the TGIC measurements was tested on several samples by injecting 10 times a solution having the same concentration, and deviations from ±1 to ±2 °C in the elution temperature were found.

RESULTS AND DISCUSSION

TGIC of polyolefins is normally carried out on a porous graphitic carbon (PGC) stationary phase with an isocratic

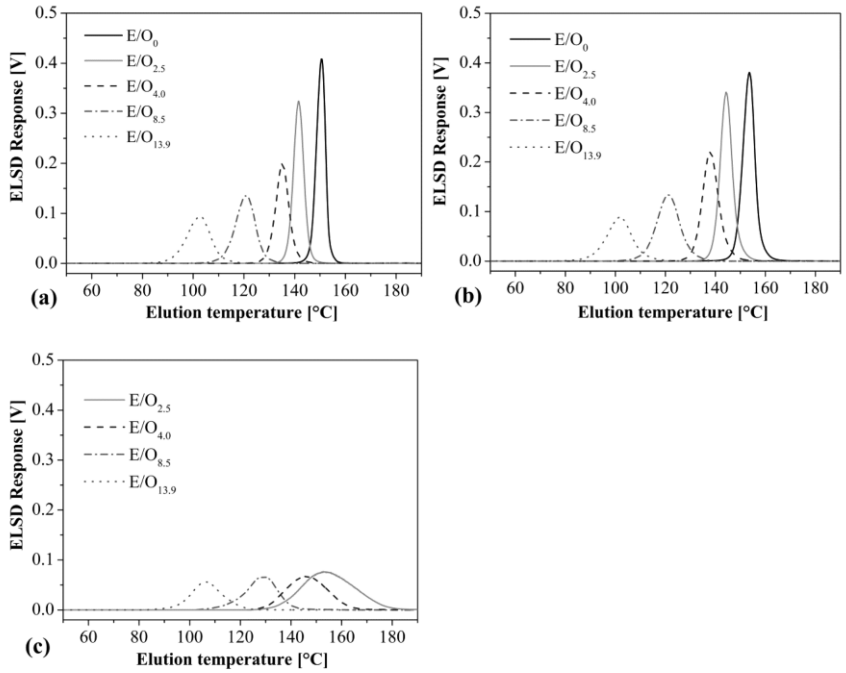

Figure 2. Chromatograms of TGIC for E/Os in (a) pure ODCB; (b) 20/80 (v/v) *n*-decane/ODCB; (c) 30/70 (v/v) *n*-decane/ODCB as the mobile phase.

mobile phase where the macromolecules are separated by their selective, temperature-controlled adsorption and desorption on the graphite surface. In this study, ODCB, TCB, 1-decanol, *n*-decane, and diphenyl ether (DPE) were chosen as mobile phase due to their substantially differing ability to dissolve[39] PE and to promote its adsorption onto PGC.[19,22,40] ODCB, TCB, and DPE can be used with an IR detector to detect polyolefins, but 1-decanol and *n*-decane pose problems, as their response interferes with that of the polyolefins. To overcome this challenge and broaden the choice of solvents for this study, instead, an evaporative light scattering detector (ELSD) has been applied that can detect polyolefins also in 1-decanol and *n*-decane as solvents. The ELSD has previously been employed as the standard detector for the separation of polyolefins via solvent gradient interactive chromatography (SGIC).[19,22,23] Table 1 shows that the ability of these solvents to dissolve PE decreases in the sequence ODCB ∼ TCB ∼ *n*-decane > 1-decanol > DPE. Additionally, previous works[19,22,23,40] have already shown that these solvents promote the adsorption of PE onto PGC in the order 1-decanol > *n*-decane > DPE > ODCB ∼ TCB.

For the first set of experiments, ODCB was chosen as the base solvent to which different amounts of *n*-decane were added. Poly(ethylene-*stat*-1-octene) (E/O) samples of varying 1-octene content were separated using the above binary solvent mixtures as TGIC mobile phase, and the chromatograms are shown in Figure 2.

In TGIC, the elution temperature signifies the ease of E/O desorption from the stationary phase. An increase in 1-octene content reduces the adsorption of the E/O chains on the graphitic surface, resulting in easier desorption and lower elution temperatures.[19,24] Figure 3 illustrates the linear relationship between the peak temperature and the 1-octene content.

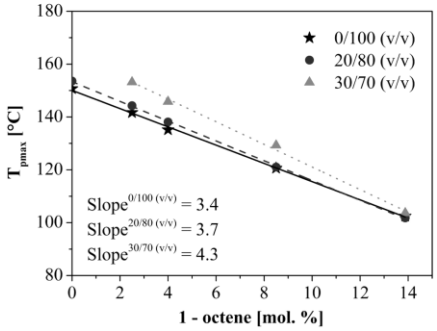

Figure 3. Elution temperature versus average content of 1-octene in the E/Os in *n*-decane/ODCB as mobile phase. Notice: Sample E/O_0 was partially retained in the column even at 170 °C in *n*-decane/ODCB at 30/70 (v/v).

The slope in Figure 3 represents the difference between the elution temperatures at peak maximum, T_{pmax}, of the E/Os, which increases with the addition of *n*-decane.

However, simultaneously the peak widths also increase (Figure 2), and with the aim to study this effect in more detail, the peaks of E/O_0 and $E/O_{2.5}$ were normalized and shifted to same T_{pmax} values in Figure 4.

To explain the above observations, it is vital to understand the effect of the mobile phase on the process of adsorption and desorption in TGIC: The polymer is injected at high temperature (e.g., 150 °C in Figure 1) and then adsorbed on the PGC surface by reducing the column temperature. Thermodynamically, in the cooling step, the system shifts from the entropy driven SEC mode (high temperature, 150 °C) to the enthalpy controlled LAC mode whereby the polymer gets adsorbed onto the PGC. The polymer is then desorbed by

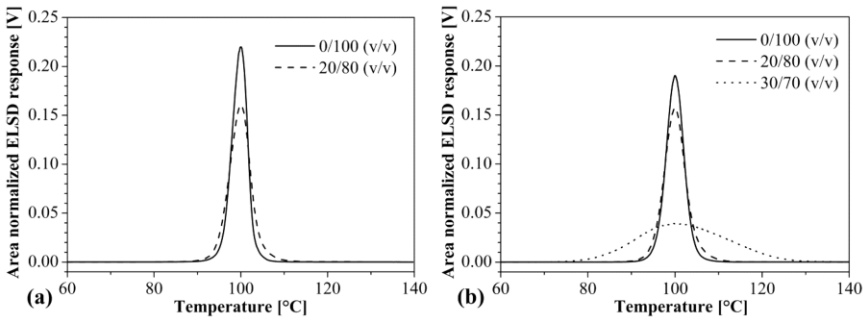

Figure 4. Peaks of (a) E/O_0 and (b) $E/O_{2.5}$ in *n*-decane/ODCB and pure ODCB. Peaks were area normalized and shifted to overlap at 100 °C on the temperature axis.

increasing the temperature in a constant flow of isocratic mobile phase. Upon raising the system temperature above desorption temperature, during the heating step, the chromatographic mode shifts then back from LAC to SEC. From literature, the transition between these two modes is known as critical conditions for chromatography (CCC)[23] where the enthalpic effects are exactly compensated by the entropic term. Desorption can thus be visualized as the transition from LAC to SEC mode with the elution occurring at CCC. This has been theoretically[41] and experimentally[42] shown for SGIC where the CCC was the mobile phase composition at which a polymer of sufficiently high molecular weight is desorbed in a solvent gradient when the column temperature is maintained constant. Analogously, in TGIC it may also be stated that in an isocratic mobile phase the temperature at which a high molecular weight homopolymer desorbs (elutes) signifies the CCC for this particular chromatographic system. Consequently, a polymer will only desorb in TGIC when the temperature exceeds the value required for CCC in a specific mobile phase. Thus, for 30/70 (v/v) *n*-decane/ODCB, the CCC temperature for E/O_0 (PE) was larger than the maximum of the temperature (170 °C) in the TGIC experiment and consequently the polymer was not desorbed. CCC for PE with PGC at 160 °C have recently been established in different mobile phases[23] and are summarized in Table 3.

Table 3. Mobile Phase Compositions at CCC for PE[a]

mobile phase	composition [v/v]
ODCB/1-decanol	90/10
ODCB/*n*-decane	80/20
TCB/1-decanol	53/47
TCB/*n*-decane	48.5/51.5

[a]Column: hypercarb. Temperature: 160 °C. Reproduced from ref 23.

This knowledge of the CCC for PE can thus be applied to select suitable binary solvent mixtures as the mobile phase for TGIC experiments. From Table 3, it can be concluded that at 30/70 (v/v) *n*-decane/ODCB, the chromatographic system is adsorption promoting until 160 °C for PE (E/O_0). The increase in strength of adsorption for PE and E/Os on PGC with addition of *n*-decane may explain the increase in their peak widths (Figure 2) due to an increased molecular weight influence in the TGIC separations. Similar increases in peak widths have also been reported for other chromatographic systems when the adsorption strength was increased in isocratic elution by increasing the oligomer/polymer chain lengths or molecular weight,[22,30,31] and in SGIC by reducing the temperature of the experiment.[43] The increase in slope of separation (Figure 3) for the case of a strongly adsorption promoting mobile phase, 30/70 (v/v) *n*-decane/ODCB, may be speculated to arise from a magnification of the selectivity of the graphitic surface due to changes in the mobile phase composition. To confirm these findings, 1-decanol was chosen, as it is a stronger adsorption promoting solvent compared to *n*-decane for PE and PGC.[23,44]

Therefore, 1-decanol was added to ODCB in various aliquots, similar to the previous experiments in *n*-decane/ODCB and TGIC was conducted with the E/Os. The addition of 1-decanol to ODCB increases the adsorption promoting ability of the mobile phase and also reduces the solvency of PE, leading to a shift of the T_{pmax} to larger values. A selectivity related increase in the slope is also observed for 10/90 (v/v) 1-decanol/ODCB (Figure 5), as was seen earlier for binary solvent mixtures of *n*-decane/ODCB (Figure 3).

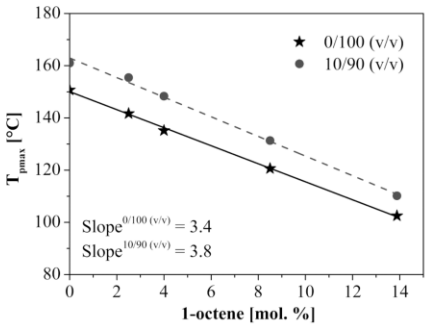

Figure 5. T_{pmax} vs 1-octene content for TGIC of E/Os in 1-decanol/ODCB as the mobile phase.

This shift of T_{pmax} to higher temperatures in binary mobile phases can be advantageously applied to separate E/Os in a larger comonomer range compared to pure ODCB, and may prove important in future for TGIC separations. Moreover, analogous to *n*-decane/ODCB experiments, the addition of 1-decanol also increases the peak widths (Figure 6) as the system becomes strongly adsorption promoting at these conditions (10/90 vol % 1-decanol/ODCB).

At concentrations of 1-decanol higher than 30 vol %, the chromatographic system is adsorption promoting to such an extent that the E/O_0 stays retained even at temperatures as high as 170 °C. The chromatographic system remains in LAC mode

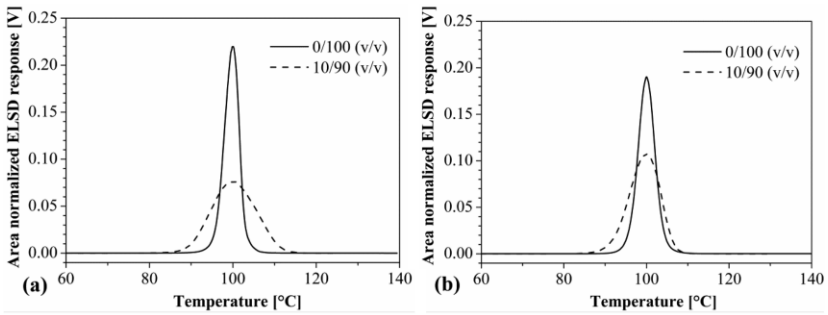

Figure 6. Peaks of (a) E/O_0 and (b) $E/O_{2.5}$ in 1-decanol/ODCB compared with pure ODCB. Peaks were area normalized and shifted to overlap at 100 °C on the temperature axis.

for the complete temperature range of the experiment and never reaches the temperature for CCC of PE (E/O_0) so that desorption could occur (CCC data, Table 3).

After stronger adsorption promoting solvents were studied, DPE was chosen as a solvent with an intermediate adsorption promoting capability to be mixed with ODCB. DPE is also weak in dissolving PE, as can be inferred from the cloud point data in Table 1. As a weak adsorption promoting agent, no increase in slope could be observed, even upon the addition of 40 vol % DPE to ODCB (Figure 7) contrary to *n*-decane/ODCB (Figure 3) and 1-decanol/ODCB (Figure 5) binary solvent mixtures observed earlier.

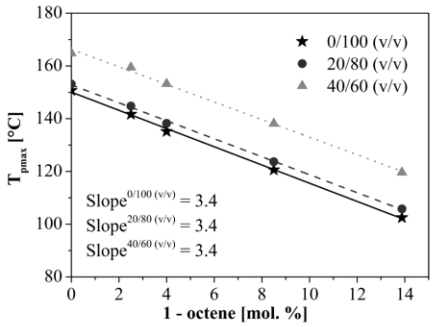

Figure 7. T_{pmax} vs 1-octene content for TGIC of E/Os using binary mixtures of DPE/ODCB as the mobile phase.

However, the E/Os desorb at elevated temperatures, which points toward a small increase in adsorption promoting effect at higher concentrations of DPE. These results are in accordance with TGIC experiments in phenol as the mobile phase, which is structurally similar to DPE.[37]

In the above discussion of the binary solvent mixtures of *n*-decane, 1-decanol, and DPE with ODCB, the increase in slope, which could lead to an improvement in resolution, was seen to be counteracted by an increase in peak width. These effects were explained to be the result of an increasing molecular weight influence and selectivity of separation in TGIC separations with stronger adsorption promoting mobile phases.

The discussion about the temperature at CCC can be used to develop other binary solvent mixtures as the mobile phase for TGIC separations. From the explanation about the TGIC adsorption/desorption process, it was concluded that the CCC temperature for a polymer has to be lower than the maximum of the temperature applied for desorption. *n*-Decane and 1-decanol cannot be applied in a pure form as the mobile phase because they are unable to desorb PE from PGC, even at temperatures as high as 200 °C. In the same sense, pure DPE is not suitable as the mobile phase for TGIC because of its high PE cloud point of 152.5 °C, which results in undesired precipitation of the PE out of the solution at lower temperatures. TCB, which has been applied earlier in SGIC and for which the CCC for PE are known (Table 3), was thus chosen as the mobile phase. TCB is known to be considerably weaker in promoting adsorption of PE onto PGC than ODCB.[22,23] Although the cloud point temperatures of PE in TCB and ODCB are similar, the latter shows slightly different selectivity for the separation of E/Os with a 1-octene content less than 9.0 mol %.

As shown in Figure 8, the T_{pmax} values of the E/Os are lower in TCB compared to ODCB, which is in conformity with its

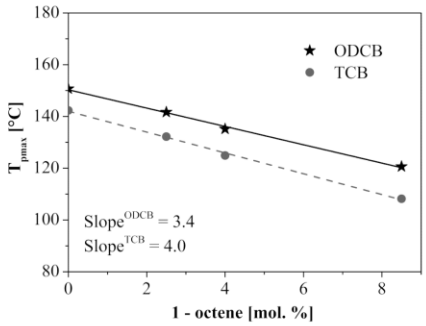

Figure 8. T_{pmax} vs 1-octene content from TGIC of E/Os in ODCB and TCB respectively.

weaker adsorption promoting nature. However, a steeper slope suggests that TCB may be more selective in the separation of E/Os (up to 9.0 mol % 1-octene content) compared to ODCB. This is in accordance to the previously reported results of TGIC experiments with TCB as the mobile phase.[38]

Applying TCB instead of ODCB may improve the selectivity for TGIC separation of E/Os having a 1-octene content of less than 9 mol % (Figure 8), but also reduces the comonomer range of the separation by lowering T_{pmax} values. However, by adding *n*-decane and 1-decanol to TCB, the comononer range of separation can be increased by shifting the T_{pmax} to higher values. The CCC in Table 3 provide a maximum content of *n*-decane and 1-decanol to be mixed with TCB for creating binary solvent mixtures of 47.5% and 51.5%, respectively. A systematic approach was used to find the optimum solvent composition by

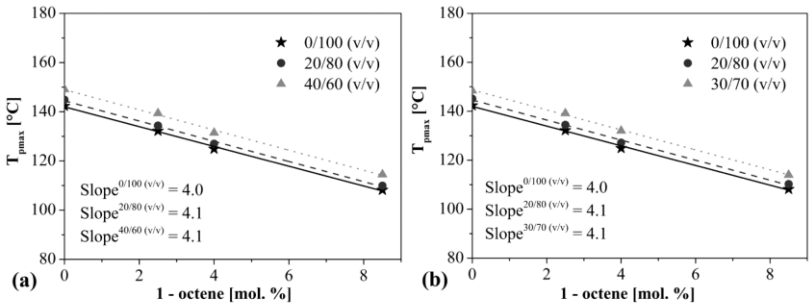

Figure 9. T_{pmax} vs the average content of 1-octene in E/Os in the mobile phase (a) *n*-decane/TCB and (b) 1-decanol/TCB.

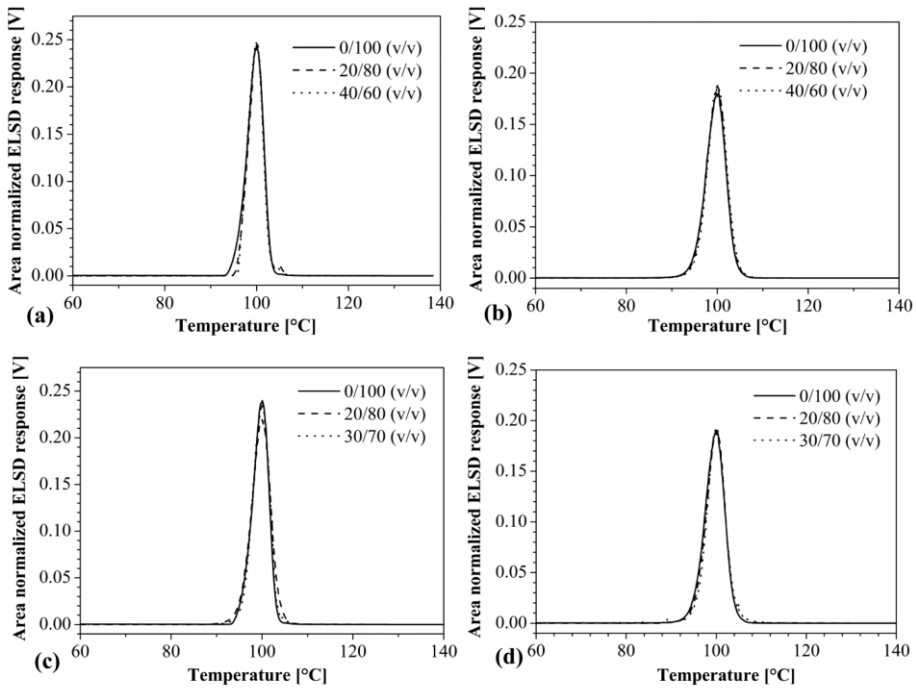

Figure 10. Overlays of chromatograms in *n*-decane/TCB (a) E/O_0 and (b) $E/O_{2.5}$; 1-decanol/TCB (c) E/O_0 and (d) $E/O_{2.5}$ compared with pure TCB. Peaks were area normalized and shifted to overlap at 100 °C on temperature axis.

addition of *n*-decane and 1-decanol to TCB in steps as the mobile phase for TGIC of the E/Os. The T_{pmax} vs 1-octene plot in Figure 9 shows a similar slope for the separation of E/Os at different concentrations of *n*-decane and 1-decanol.

This is an effect similar to addition of DPE to ODCB where DPE was not strong enough to significantly change the ability of ODCB to promote PE adsorption onto PGC. Analogously, in this instance too, the adsorption promoting ability for TCB is extremely weak, so the overall adsorption promoting ability of the binary solvent mixture remains unchanged, even on the addition of higher volumes of stronger adsorption promoting solvents, i.e., 40 vol % *n*-decane and 30 vol % 1-decanol. The separation between the E/O peak maxima obtained from the slope of T_{pmax} vs 1-octene content plot (Figure 9) in these binary solvent mixtures is comparable to pure TCB, but is significantly increased compared to pure ODCB (slope at 3.4, Figure 8).

Additionally, no increase in the peak width is observed (Figure 10), as the chromatographic system is not yet strongly adsorption promoting for the temperature range of the TGIC experiment.

$E/O_{13.9}$ has not been included in the T_{pmax} vs 1-octene plot (Figure 9) as it showed partial adsorption. TCB is not strong enough to support full retention of $E/O_{13.9}$, i.e., part of the sample with high content of 1-octene eluted without being adsorbed onto PGC, while a part of the sample with a lower content of 1-octene was retained on the PGC and eluted at higher temperatures. Adding a higher volume of *n*-decane or 1-decanol into TCB made the system strongly adsorption promoting and yielded results similar to 30/70 (v/v) *n*-decane/ODCB and 10/90 (v/v) 1-decanol/ODCB.

The above-described TGIC measurements suggest that addition of *n*-decane/1-decanol to ODCB results in an increase of the E/O peak separation and peak width. It has been known that the chromatographic resolution (R) depends upon both these parameters and can be calculated from eq 1:[5,45]

Table 4. Resolution (R) from Peak Width at Half Height (w) and T_{pmax} for TGIC of E/Os in Different Mobile Phases

		w		T_{pmax} (°C)			R
mobile phase	(v/v)	E/O_0	$E/O_{2.5}$	E/O_0	$E/O_{2.5}$	slope[a]	$(E/O_0 - E/O_{2.5})$
ODCB	100	4.2	4.6	150.7	141.7	3.4	1.20
n-decane/ODCB	20/80	5.4	5.6	153.6	144.3	3.7	0.99
1-decanol/ODCB	10/90	12.9	8.8	161.0	152.4	3.8	0.47
DPE/ODCB	20/80	4.2	4.7	153.4	144.8	3.4	1.14
	40/60	4.3	5.1	164.8	158.4	3.4	0.80
TCB	100	4.1	4.6	142.3	132.2	4.0	1.36
n-decane/TCB	20/80	4.1	4.6	144.8	134.3	4.1	1.42
	40/60	4.2	4.7	149.1	137.9	4.1	1.48
1-decanol/TCB	20/80	4.2	4.6	145.1	134.5	4.1	1.42
	30/70	4.2	4.7	148.4	137.2	4.1	1.48

[a]Slope from T_{pmax} vs 1-octene content (mol %) in TGIC of E/Os on PGC.

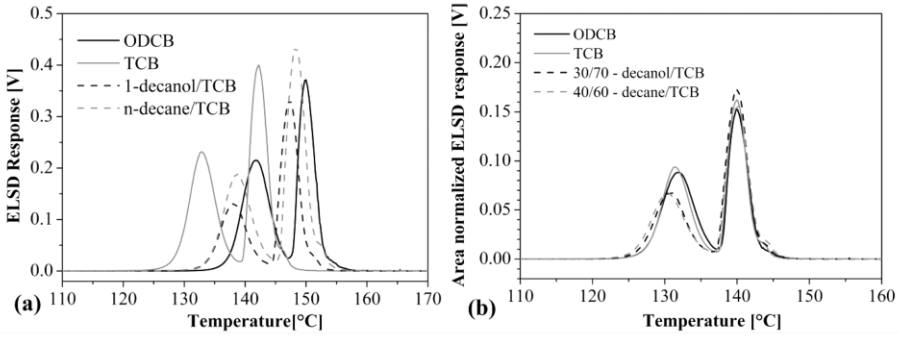

Figure 11. Overlay of chromatograms corresponding to blend $E/O_{0.3}$ and $E/O_{2.5}$ mobile phase: ODCB, TCB, 30/70 (v/v) 1-decanol/TCB, and 40/60 (v/v) *n*-decane/TCB. (a) Unmodified chromatography. (b) Peaks were area normalized and elution volume shifted to the same temperature.

$$R = \frac{2[T_{pmax(x)} - T_{pmax(y)}]}{1.7[w(x) + w(y)]} \quad (1)$$

Where T_{pmax} (x) and T_{pmax} (y) correspond to the elution temperature (or volume) T_{pmax} and $w(x)$ and $w(y)$ are equal to the peak width at half height for samples E/O_x and E/O_y, respectively. An R value of 1.5 implies that the two peaks considered are baseline resolved, with smaller values indicating lesser separation. The values for T_{pmax} and w of E/O_0 and $E/O_{2.5}$ in the tested mobile phases are summarized in Table 4.

The addition of *n*-decane, 1-decanol, and DPE to ODCB leads to a decrease in chromatographic resolution, whereas the addition of *n*-decane and 1-decanol to TCB shows an opposite effect. From Table 4, the calculated resolution values in binary solvent mixtures 40/60 (v/v) *n*-decane/TCB and 30/70 (v/v) 1-decanol/TCB are observed to be 1.48 in value. The R values in these two binary solvent mixtures are closest to 1.5, which signifies a baseline resolution, and are hence concluded to be an optimized system for TGIC based separation of E/Os.

To confirm the applicability of these optimized binary solvent mixtures, a model blend of $E/O_{0.3}$ and $E/O_{2.5}$ in a ratio 1:1 by wt (Table 2) was separated. Figure 11 shows the overlay of chromatograms from the TGIC experiments in ODCB, TCB, 40/60 (v/v) *n*-decane/TCB, and 30/70 (v/v) 1-decanol/TCB.

An increase in the T_{pmax} values of TCB with the addition of 1-decanol and *n*-decane can be clearly observed (Figure 11a). Figure 11b shows the improvement in the resolution of TGIC based E/O separation in the optimized binary solvent mixtures 40/60 (v/v) *n*-decane/TCB and 30/70 (v/v) 1-decanol/TCB compared to routinely used ODCB, as was predicted by the calculations.

CONCLUSION

Mobile phase composition plays a crucial role in TGIC based polyolefin separations. To attain a deeper understanding of its role, different solvents have been applied in pure form and in mixtures with systematically varied proportions, and the corresponding resolutions in the TGIC separation of poly(ethylene-*stat*-1-octene) (E/O) have been studied. For the first time, alkanes and alcohols have also been applied as the mobile phase for TGIC separations along with IR transparent solvents like ODCB, TCB, and DPE with the help of an evaporative light scattering detector. To understand the effect of the mobile phase composition, the concept of critical condition for chromatography (CCC) was applied. Previously gained knowledge about CCC of PE in these solvents was made use of with the aim to select optimized binary solvent mixtures for TGIC. Addition of *n*-decane or 1-decanol to ODCB as a TGIC mobile phase made the chromatographic system more adsorption promoting for PE onto the porous graphitic carbon (PGC) stationary phase. This resulted in an increase in the separation between the peak maxima through higher selectivity, and broader peaks, possibly due to larger molecular weight influence on the separation. DPE was taken as a representative of solvents that are both weak in terms of dissolving PE and promoting adsorption of PE onto PGC. Application of DPE in a binary solvent mixture with ODCB resulted in no improvement in resolution. TCB was applied as a TGIC mobile phase because it leads to a larger resolution of E/O

separations compared to ODCB when their 1-octene content is below 9 mol % and this could then be further improved by the addition of *n*-decane or 1-decanol to TCB as the TGIC mobile phase for E/O separations. With the help of resolution calculations, 40/60 (v/v) *n*-decane/TCB and 30/70 (v/v) 1-decanol/TCB were concluded to be the optimized binary solvent mixtures that could maximize the resolution of TGIC based E/O separations. The improvement in the resolution with these optimized binary solvent mixtures was experimentally verified by separating a model blend of two representative E/Os by TGIC. In summary, binary solvent mixtures show great application potential as the mobile phase for TGIC, which could be improved even further by using quantitative detectors (e.g., NMR), as the response of the evaporative light scattering detector used in this study depends on a number of factors like molecular weight and composition of the polymer.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This research forms part of the research collaboration between Material Analytics Group, Fraunhofer Institute, LBF, Darmstadt and the Dow Chemical Company, USA. The authors acknowledge the fruitful discussions with Drs. M. Miller, W. Winniford, J. Lyons, and D. Lee of the Dow Chemical Company.

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6.5 Investigating interactions of polyethylene with graphite in the presence of solvent

Carbon-based sorbents (various types of graphite) have been applied recently with great success as stationary phase in HT-LAC to separate polyolefins according to their chemical composition and microstructure[73-77]. However, the fundamentals behind the interaction of polyethylene (PE) from solvents onto the graphite surface need to be understood in order to understand the separation mechanism in HT-LAC. To achieve this goal NMR can be applied in a unique manner. NMR spectroscopy is not only one of the most important methods for structure elucidation; it is also well-established as a quantitative reference method[150]. Changes in the analyte concentration of a solution as a result of crystallization or adsorption, for example, result in a reduction of signal intensity in the spectrum which can be monitored online without calibration.

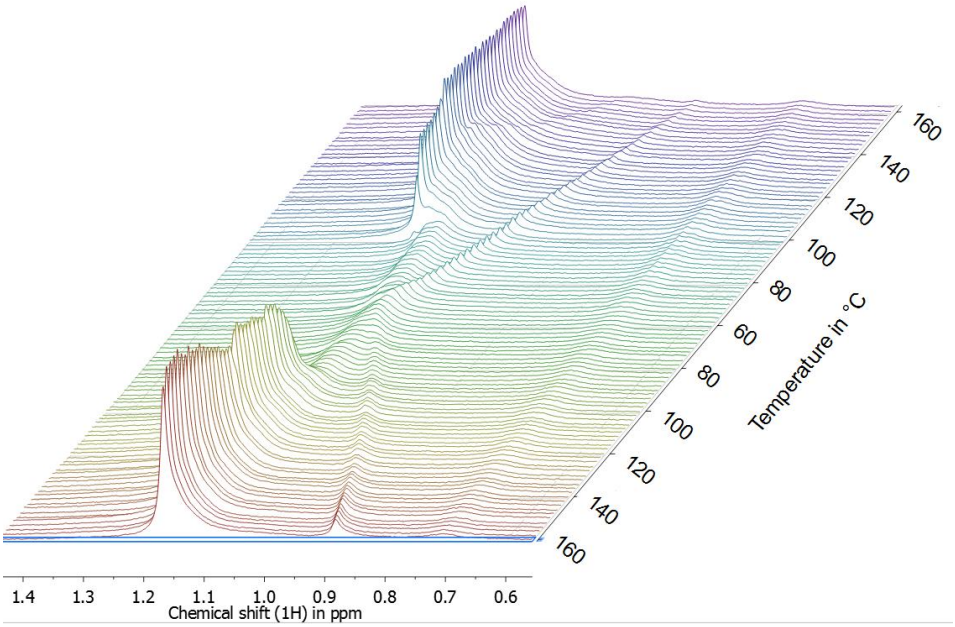

Figure: TG-NMR of HDPE (MW= 115.5 kg/mol) in the temperature range 160→60→160 °C with 2 °C steps.

Recently temperature gradient HT-NMR (TG-NMR) has been developed to monitor the heterogeneity of polyolefins with regard to unsaturation[152, 164]. In this work we show how TG-NMR using optimized experimental parameters can be applied to study the interactions between PE and graphite in the presence of ODCB as solvent when the temperature is varied. Various techniques like HT-TGIC, CEF and solution DSC were used to complement the TG-NMR experiments as part of this study and the interactions between PE and graphite were concluded to be of adsorptive nature.

Studying the interactions of polyethylene with graphite in the presence of solvent by High Temperature Thermal Gradient Interactive Chromatography, Thermal Gradient Nuclear Magnetic Resonance Spectroscopy and Solution Differential Scanning Calorimetry

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ABSTRACT

High temperature thermal gradient interactive chromatography (HT-TGIC or TGIC) has emerged as an important analytical tool to determine the comonomer content distribution (CCD) present in homo- and copolymers of polyethylene (PE). The method separates the macromolecules according to the differences in their interactions, in solution, with a graphite stationary phase using temperature as a variant. It is vital to gain insight into the nature of these interactions in order to further improve the separation resolution, and increase the accuracy of CCD measurement. Nuclear magnetic resonance (NMR) spectroscopy has been routinely applied for quantitative determination of comonomer content in olefinic copolymers. In this paper NMR has been adapted in a unique manner to monitor the temperature dependent concentration of PE in solution in the presence of nano-graphite (NG). It was found that in the presence of NG, a decrease in polymer concentration can be observed for both a semicrystalline PE homopolymer, and a highly amorphous poly (ethylene-*stat*-1-octene) with 37 wt. % 1-octene content (E/O_{37}), upon reducing the temperature. The reduction observed for

the homopolymer started at a temperature significantly above its crystallization temperature from solution. A similar reduction was also observed for the highly amorphous E/O_{37}. This decrease was found to be reversible upon heating, with the absence of any hysteresis which gives an evidence for an adsorption/desorption mechanism in the system polyolefin/graphite/ODCB. Solution DSC experiments carried out at comparable conditions showed no exothermic event at the temperature where the decrease was observed in TG-NMR, thus excluding induced crystallization as the underlying mechanism. As a result, the mechanism of interaction between the graphite surface and the macromolecules can be concluded to be based on adsorptive interactions. The temperature of the reduction in concentration of PE homopolymer and E/O_{37} observed in TG-NMR matched the elution temperature in TGIC under similar experimental conditions which confirmed the TGIC separation mechanism as based on adsorption without any influence of induced crystallization. Another interesting finding was the mobility of PE macromolecules observed at temperatures significantly below the crystallization point in dilute solution by ^{1}H NMR.

KEYWORDS

Thermal gradient NMR, TGIC, polyethylene, graphite, adsorption, crystallization, Solution DSC

INTRODUCTION

Polyolefins, with their excellent cost/performance ratio, are by volume the most produced synthetic polymers with a global production of 147 million tons in 2011 and a predicted growth to 170 million tons by 2017[1]. Consequently, these materials are being adapted to many novel and diverse applications through the development of new catalyst systems[2-5] and process technologies[6] that increase cost effectiveness and enable greater control over macromolecular microstructure. The above has been made possible by an increase in knowledge about their molecular structure→property relationships as a result of advances in analytical techniques.[7-16] The molecular heterogeneities of polyolefins can be classified to a large extent by their comonomer content (CC), comonomer content distribution (CCD), molecular weight (MW), molecular weight distribution (MWD), as well as content and distribution of long chain branching (LCB). MW and MWD are determined routinely by high temperature size exclusion chromatography (HT-SEC).[17,18] The LCB content in polyolefins can be retrieved from ^{13}C nuclear magnetic resonance (NMR) spectroscopy,[19,21] multi-

detector SEC[19,20] and rheology.[20-23] The average CC of polyolefins is determined with the help of spectroscopic techniques like Fourier transform infra-red (FTIR)[24,25] and NMR.[26] NMR is also a powerful technique for structure elucidation and delivers information about unsaturation[27-29] and microstructure, such as tacticity,[30] inverse insertion[31] and comonomer sequence distribution.[32] A particular advantage is the ability of NMR to quantify without the necessity of calibration as the primary technique.[33]

Apart from the CC it is essential to analyze the CCD as it directly impacts the final properties and, in turn, the end-use versatility of polyolefins. For CCD analysis, crystallization based techniques such as temperature rising elution fractionation (TREF),[8] crystallization analysis fractionation (CRYSTAF)[11] and, more recently, crystallization elution fractionation (CEF)[34] have been used. However, crystallization based techniques suffer from the limitations caused by co-crystallization,[35] and a narrow useful range of comonomer content (0 to ~ 9 mol %). The application range of the crystallization based techniques may be extended up to ~ 13 mol % by using cryogenic cooling techniques, but the freezing point of the solvent 1,2-dichlorobenzene (ODCB) may set a limit to this strategy. Recently, high temperature liquid adsorption chromatography (HT-LAC) using porous graphitic carbon (PGC) as stationary phase[12-16] has emerged as an alternative for CCD determination. Depending on the variant which governs the separation, HT-LAC can be classified into solvent gradient (SGIC) and thermal gradient (TGIC) interactive chromatography. In SGIC, [12-16] the CCD of polyolefins is determined by selectively separating them in a solvent gradient with a stationary phase at isothermal conditions, while in TGIC[36,37] the separation is achieved by using a thermal gradient and an isocratic mobile phase in general. SGIC offers the capability to separate over the full range of comonomer content, but is limited with regard to the choice of detectors with the evaporative light scattering detector (ELSD) as the sole option. An ELSD suffers from non-linear dependence on sample concentration as well as on solvent composition.[38, 39] Even with careful calibration of its response, it is extremely difficult to obtain quantitative results with the ELSD. TGIC, on the other hand can use various detectors like infra-red (IR) detector, light scattering detectors and differential viscometers, to quantitatively determine the CCD of polyolefins comprehensively.[36, 37]

TGIC also provides the advantage of a larger comonomer range of application (up to 33 mol % 1-octene) compared to crystallization based techniques (up to 9 mol % 1-octene), in

ODCB.[36, 37] However, TGIC also suffers from the limitations in resolution when using graphite as substrate, as its resolution is about half of that from CEF or TREF[40, 41] for the comonomer content range (~ 0 - 9 mol %) where both techniques may be applied. Therefore, improving the resolution in TGIC is essential to fully exploit its application potential and a key step towards this goal is to gain insight into the fundamentals of its underlying adsorption/desorption mechanism. For this it is vital to study the nature of interaction between the polymer and the stationary phase i.e., the graphite surface, in the presence of the mobile phase. Theoretical and experimental studies have shown that the interactions between alkanes and graphite in the presence of solvents are based upon London dispersion forces.[42-47] However, as explained earlier, homopolymer polyethylene (PE), although similar in structure to alkanes, exhibits tremendous complexities in terms of its various molecular heterogeneities and, additionally, high temperatures are needed for its dissolution. This has led to the difficulties in studying the interaction behaviour of PE on a graphite surface in the presence of solvents that are commonly used in liquid chromatographic separations. To fulfil the above necessity in this paper, the interactions between PE and graphite that occur in TGIC in the presence of a solvent will be investigated with the help of ^{1}H NMR. Zhou et al. recently pioneered the thermal gradient NMR (TG-NMR) methodology[28, 48] to quantify unsaturation of polyolefins in solution by ^{1}H NMR at variable temperatures. In this work, experimental parameters for the TG-NMR will be developed to monitor the temperature dependent equilibrium concentration of PE and poly (ethylene-*stat*-1-octene) in ODCB, with and without the presence of graphite. Particular attention will be given to the question of whether the mechanism underlying the separation of ethylene copolymers in TGIC is based on induced crystallization or adsorption and desorption. The various conclusions about the mechanism of interaction between the olefinic macromolecules and the graphitic surface will be also supported with the help of solution differential scanning calorimetry.

EXPERIMENTAL

Polymers

PE, having a weight average molecular weight (M_w) of 115 kg/mol (PE_{115}) and a dispersity of 1.4, was purchased from Polymer Standards Service, Mainz, Germany. Poly (ethylene-*stat*-1-octene), having a M_w of 26 kg/mol and containing 37 wt. % of 1-octene (E/O_{37}), and a dispersity of 2.2, was obtained from The Dow Chemical Company, USA

Thermal Gradient Interactive Chromatography (TGIC)

A commercial CEF instrument (Polymer Char, Valencia, Spain) was used to perform the TGIC measurements.[37] A 4.8 x 80 (mm) IDxL stainless steel column packed with glass beads of a diameter of 20-27 µm (MO-SCI Specialty Products, LLC, Rolla, MO, USA) was installed in front of the infra-red (IR) detector (Polymer Char, Valencia, Spain) in the top oven of the CEF instrument. The experimental parameters that were applied are tabulated below.

Table 4: TGIC experimental parameters

Experimental parameter	Setting
Top oven/Transfer line/Needle temperatures	150 °C
Dissolution temperature	150 °C
Dissolution stirring*	2
Sample loading volume	0.4 mL
Pump stabilization time	5 s
Pump flow rate of column cleaning	0.5 mL/min
Pump flow rate of column loading	0.3 mL/min
Stabilization temperature	150 °C
Stabilization time (pre/before column load)	3.0 min
Stabilization time (post/after column load)	1.0 min
Soluble fraction (SF) time	3.0 min
Cooling rate	3.00 °C/min
Cooling temperature range	150 °C → 30 °C
Cooling flow rate	0.00 mL/min
Heating rate	2.00 °C/min
Heating temperature range	30 °C → 160 °C
Heating/elution flow rate	0.500 mL/min
Isothermal time at 160 °C	10 min

**0 – No stirring, 1 – medium stirring, 2 – high stirring*

Samples were prepared by heating at 160 °C for 60 minutes at a concentration of 4.0 mg/ml in ODCB (defined below).

Silica gel 40 (EMD Millipore, Billerica, MA, USA) was dried in a vacuum oven at 160 °C for about two hours prior to use as a dehydrating agent. 0.8 grams of 2,5-di-ter-butyl-4-methylphenol (BHT, Sigma-Aldrich, St. Louis, MO, USA) and 5.0 grams of silica gel were added to two liters of 1,2-dichlorobenzene (ODCB, 99 % anhydrous grade, Sigma-Aldrich, St. Louis, MO, USA). This "ODCB containing BHT and dehydrated with silica gel" is now referred to as "ODCB". It was then sparged with dried nitrogen for one hour prior to use.

The detailed methodologies of data processing and calibration were according to the Ref.[49] Eicosane (IUPAC: Icosane) (Sigma-Aldrich, St. Louis, MO, USA), and PE, M_w =120 kg/mol (PE_{120}) were used as internal standards for calibration. The peak elution temperature of eicosane was 30 °C and that of PE was 150 °C.

Nano-graphite powder (NG) was obtained from Sigma Aldrich (Netherlands) with a reported average particle diameter < 50 µm, BET surface area >100 m^2/g and relative density 0.25 – 0.6. The NG was crudely sized by sedimentation in methanol and decanting the supernatant after ~ 60 seconds. The latter was dried overnight at room temperature, and added to the empty stainless steel column using the tap-fill method.

A TGIC column was packed with NG according to Ref.[16] The column was made of 316 stainless steel "Hieff" (Grace Discovery Sciences, Columbia, USA) with dimensions of 5.3 x 30 (mm) IDxL. The end caps were stainless steel with 2 µm porosity stainless steel frits (Valco).

The packed column was then purged with ODCB at room temperature at a flow rate of 0.1 mL/min for one hour. The flow was increased to 0.5 mL/min and the column was heated to 160 °C at 10 °C/min. The column was purged for 30 minutes at this condition, and then cooled to 120 °C prior to the first injection.

Crystallization Elution Fractionation (CEF)

A commercial CEF instrument (Polymer Char, Valencia, Spain) was used to perform the experiments. An IR5 detector (Polymer Char, Valencia, Spain) was applied for all experiments. ODCB similar to TGIC experiments was applied as solvent. The experimental parameters were set according to Ref.[50]

Thermal Gradient Nuclear Magnetic Resonance (TG-NMR)

Due to sensitivity concern, ^{1}H NMR was used. All ^{1}H NMR measurements were carried out on a Varian (Palo Alto, US) Mercury-VX 400 NMR spectrometer (9.4 T) using a 10 mm probe. The ^{1}H NMR spectra were acquired at a Larmor frequency of 400.13 MHz with a 90° excitation pulse, 17.5 s relaxation delay to ensure quantitative NMR results, 64K time domain points (corresponding with an acquisition time of 2.3 s at a spectral width of 6.4 kHz). Fourier transformation was done after zero filling to 64K data points in the frequency domain and an exponential filtering of 0.3 Hz. Phase and baseline correction were done manually.

A sample was dissolved in ODCB at a concentration of 0.1 mg/mL for the TG-NMR experiments. 100 mg NG were added to the sample for conducting TG-NMR experiments with graphite. No stabilizers (e.g., phenolic or phosphitic antioxidants) or relaxation agents like chromium (III) acetylacetonate, $Cr(acac)_{3,}$ were added to exclude possible superposition of their proton signals with those of the analyte in the ^{1}H NMR spectra and/or experimental complications. The head space of the NMR sample tube was flushed with nitrogen to avoid degradation of the polymer sample at elevated temperatures.

Poly (dimethylsiloxane), PDMS, with M_w of 16 kg/mol and a dispersity of 1.04 was purchased from Polymer Standard Services (Mainz, Germany) and dissolved in ODCB-d_4. The change in temperature during the TG-NMR experiment resulted in a variation of the tuning/matching of the NMR probe which manifests as a decrease in intensity of all signals in the spectra. Hence, PDMS was used as a coaxial insert to provide an external intensity standard for all TG-NMR experiments.

The TG-NMR experiments were acquired using a temperature array with 2 °C per step. At each step 64 scans were taken and the resulting spectra were analyzed with identical phase/baseline correction. The flow rate of the temperature control gas (here nitrogen) was set to 15 L/min. A pre-acquisition delay of 60 s was used to allow the temperature to equilibrate

at each temperature step. The delay was determined with the temperature calibration standard. To achieve quantitative results, a detailed spin-lattice relaxation time (T_1) for the polyolefin solution with, and without, graphite was studied[51] and all the studies reported in this paper were with a relaxation delay of at least 5 x T_1.

Solution Differential Scanning Calorimeter (Solution DSC)

Solution DSC experiments were conducted with a C80 micro-calorimeter from SETARAM Instrumentation (Caluire, France). The thermodynamic events occurring in the sample solution were detected by a 3D Calvet sensor which completely surrounds the sample volume. The sample concentration for the experiments was 10 mg/mL. The cooling rate was maintained constant at 0.1 °C/min. The sample solution was first measured without graphite, and then in the presence of 100 mg NG.

RESULTS AND DISCUSSION

The interaction of polyolefins with a stationary phase in the presence of a mobile phase through temperature control forms the basis for studying their CCD by TGIC. A better understanding of these interactions is important to further improve the separation resolution. In TGIC the sample is injected at high temperature (150 °C) and then adsorbed onto the graphitic surface by lowering temperature. The adsorbed sample is next desorbed by elevating the temperature in a constant isocratic flow of mobile phase. Various forms of graphite have been tested as stationary phase, with porous graphitic carbon, commercially available as Hypercarb™, being widely used.[12-16] However, all of these tend to settle in ODCB due to their density, thus rendering the investigation by TG-NMR impossible. Therefore, for the study undertaken here, nano-graphite (NG) was chosen, which due to its flaky and small-particle-size nature remains suspended in ODCB. Figure 1 shows the TGIC experiment on PE having an M_W of 115 kg/mol (PE_{115}) with ODCB as mobile phase using a column packed with NG. Eicosane and PE_{120} were added as internal standards.

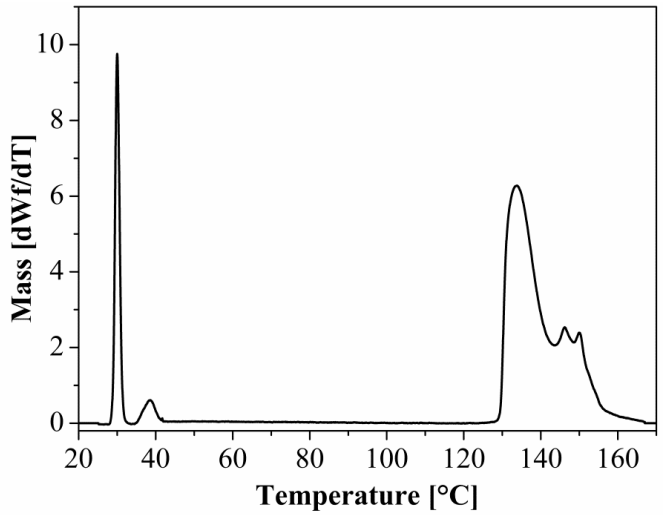

Figure 1: TGIC chromatogram of PE_{115} (with eicosane and PE_{120}) by using the NG column with ODCB as mobile phase. Concentration: 2 mg/mL. Experimental conditions as in Table 1.

In Figure 1 it can be seen that the eicosane and PE_{120} eluted with their temperature of peak maxima (T_{pmax}) at 30 °C and 150 °C respectively. The 2nd small peak with a T_{pmax} of ~ 40 °C can be assigned to an unretained fraction of the PE_{115} with low molecular weight which elutes without interaction with the NG surface. The elution of PE_{115} occurs between 130 – 160 °C with a T_{pmax} of ~ 135 °C. An unsymmetrical peak shape was observed at 120 – 160 °C (tailing) which can be the result from overloading.

As was explained earlier it may be expected that the decrease in temperature would lead to an increase in adsorptive interactions between the macromolecules and the graphite, but the same is also true for the crystallization of PE in presence of a solvent. It is well known that the T_{pmax} of PE in TGIC is significantly higher compared to its T_{pmax} from crystallization elution fractionation (CEF).[40] The difference in T_{pmax} values suggests differences in the type of interactions between TGIC and CEF separations, but the exact nature of these needs to be explored, and the recently developed Temperature Gradient NMR (TG-NMR)[28, 48] was applied for this purpose.

For the TG-NMR experiments a homopolymer PE_{115} was chosen. The temperature range of cooling was selected as 160 – 30 °C, similar to that in TGIC experiments. The solvent for these TG-NMR experiments was ODCB-d_4, analogous to the TGIC mobile phase. A NG with a relative density (r.d.) of 0.25 - 0.6, lower than ODCB-d_4 (r.d. of 1.3), was chosen as it stayed suspended in solution in the NMR tube for the entire duration of the TG-NMR experiments.

In these TG-NMR experiments the sample was prepared by dissolving PE_{115} in ODCB at a low concentration of 0.1 mg/mL which enables the detection of small differences arising from the various interactions. First the sample was measured without NG, and later 100 mg of NG were added to the same NMR tube for the TG-NMR studies in the presence of graphite. The sample was placed in the NMR probe, and a temperature array from 160 → 30 °C with 2 °C steps was programmed. For quantification the proton signal intensities were determined by integrating the corresponding signals (peak area) in the ^{1}H NMR spectra. Figure 2 shows the ^{1}H NMR spectrum of the PE_{115} sample at 140 °C with peak assignments.

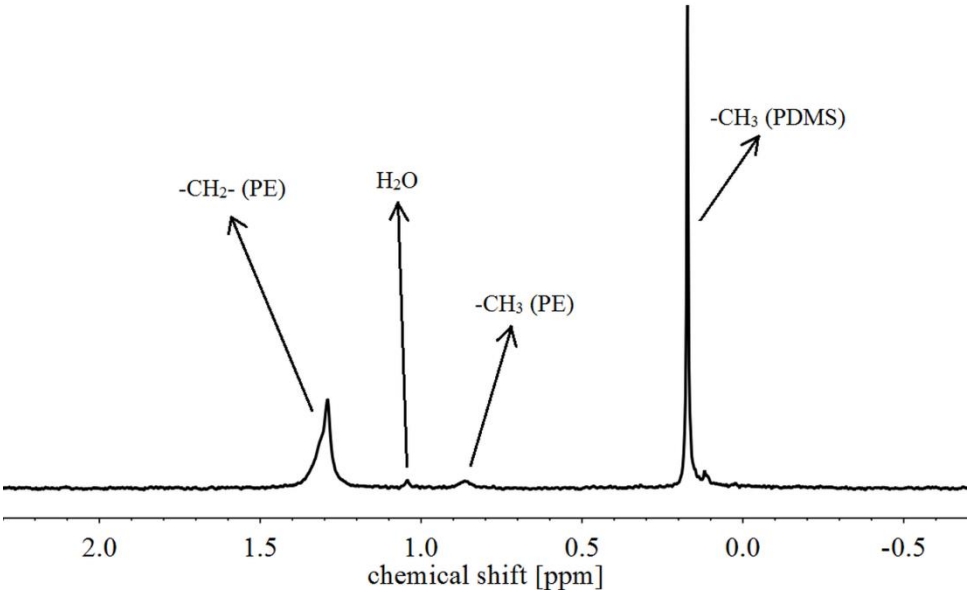

Figure 2: ^{1}H NMR spectrum of PE_{115} with coaxial insert. Spectrum zoomed to the aliphatic region. Temperature: 140 °C.

In Figure 2 the intense resonance at 1.29 ppm belongs to the methylene (-CH_2-) group of the backbone, and the weak signal at 0.85 ppm to the methyl (-CH_3) protons on the end group of PE_{115}. The small signal at 1.05 ppm originates from a minute amount of water present in the solvent (ODCB-d4). The water signal shifted downfield, moving across the methylene peak, from 1.01 ppm at 160 °C to 1.37 ppm at 30 °C. Therefore, to accurately quantify the PE_{115} signals, the total integration range from 2.0 ppm to 0.5 ppm was taken; the water signal was quantified and subtracted for all temperatures. An intense resonance from the protons of the methyl groups of the external PDMS standard can be seen at 0.17 ppm. An integration range of 0.7 ppm to -0.5 ppm was applied for the quantification of signal intensities from the methyl groups in PDMS.

Using the above integration ranges, Figure 3 shows the normalized intensities for PE_{115} versus temperature using the above integration ranges with and without the presence of NG.

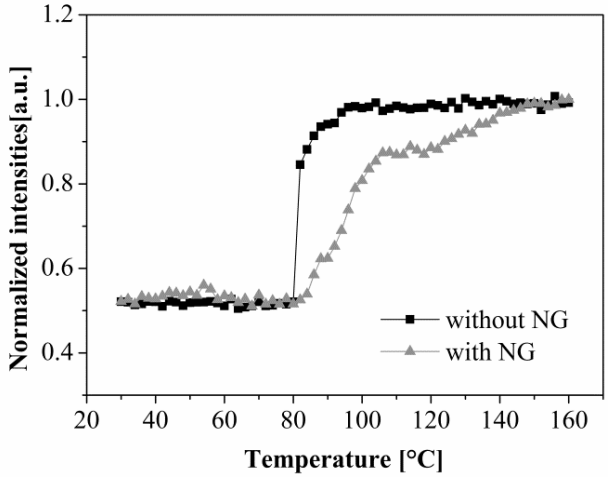

Figure 3: Normalized intensities of (-CH_2- + -CH_3-) PE_{115}/ (-CH_3) PDMS in TG-NMR experiments using ODCB-d4 and a temperature array from 160→30 °C in 2 °C steps. Note: protons from water were corrected for all temperatures.

Figure 3 shows the integrated normalized signal intensities from the methyl and methylene groups of PE with respect to the signal intensities of methyl groups from PDMS at each decreasing temperature step of the array. As this plot will be applied to interpret the interactions of the system polymer/NG/ODCB at variable temperatures it is vital to understand the principle that governs the detection of these signal intensities. Generally, in solution state ^{1}H-NMR spectroscopy only the protons present in the liquid phase are detected. The proton signals may broaden considerably and become impossible to distinguish from the baseline if the mobility of polymer segments decreases as a result of either adsorption onto the graphite or crystallization. Thus the PE molecules which are in solid state or strongly adsorb or crystallize onto graphite are undetectable by solution NMR, reducing the overall PE proton signal intensity in the sample. By monitoring the reduction of proton signal intensities from the PE_{115} with decreasing temperature the disappearance of polymer chains out of the solution can be quantified.

In the absence of NG (Figure 3), the signal intensity of the PE_{115} is observed to decrease sharply at ~ 80 - 90 °C. PE_{115} molecules crystallized from the solution into the solid phase and, hence, a sharp reduction in proton signal intensity is observed between 80 - 90 °C. Similar crystallization temperatures were also observed in cloud point[51] and CRYSTAF[11]

experiments conducted earlier for homopolymer PE in ODCB. In the presence of NG, the PE_{115} signal showed a similar sharp decrease at 80 – 100 °C. Surprisingly, independent from the presence of NG, the signal intensity of the PE_{115} did not completely reduce to zero values even at 30 °C, and almost 50 % of the initial proton signal could still be detected. Since the protons from the water signals were subtracted, this residual proton signal at room temperature must originate from the segments of PE_{115} that are still sufficiently mobile to be detected. This 50 % residual signal intensity may belong to the small amount of low M_w PE chains that are soluble at 30 °C, as 1 - 3 % of the PE_{115} sample are soluble at room temperature in ODCB. To study this residual PE_{115} signal intensity in detail, CEF experiments were performed under similar sample concentration. In CEF the polymer in a solution of particular concentration is injected at high temperature (145 °C) and then crystallized in a column packed with glass beads while lowering the temperature. The crystallized sample is next eluted by elevating the temperature in a constant flow of isocratic mobile phase as the polymer re-dissolves at specific temperatures and are detected with an IR detector. Figure 4 shows the CEF experiments conducted on PE_{115} in ODCB at the same concentration as was used in the TG-NMR experiments.

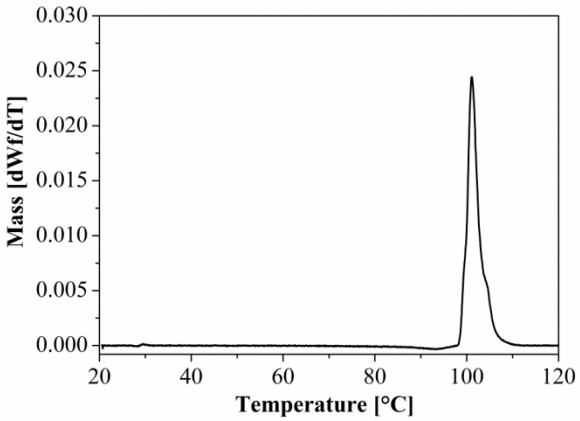

Figure 4: CEF plot of PE_{115} in isocratic ODCB as mobile phase. The experimental parameters were set according to Ref.[50] Concentration: 0.1 mg/mL.

CEF showed the presence of only 3.7 % of in PE_{115} sample still in solution around 30 °C which doesn't account for the 50 % residual PE_{115} signals that were detected in Figure 3. It could be speculated that the rest of the 50 % residual intensity of the PE signal originates from the PE being in a crystallized but quasi-mobile state in the ODCB-d_4 with the macromolecules being crystallized as shown by the CEF, but few macromolecular chain segments still being mobile enough to be detected by the ^{1}H NMR.

More interestingly, in the presence of NG, a second shallower decrease in PE_{115} signal intensity is also observed from ~ 150 °C (range: 100 – 150 °C). This is a significant observation as this temperature coincides with the T_{pmax} from TGIC (Figure 1) and may explain the interactions occurring in these chromatographic separations. There could be three possible explanations: (1) PE_{115} adsorption onto NG, (2) an unstable thermodynamic equilibrium existing in the NMR tube or (3) crystallization induced by NG at elevated temperatures. To test the possibility of the thermodynamic equilibrium of the process a TG-NMR experiment was performed in a temperature array 160 °C → 80 °C in steps of 20 °C with three ^{1}H-NMR spectra acquired in 30 minutes intervals at each temperature (Figure 5).

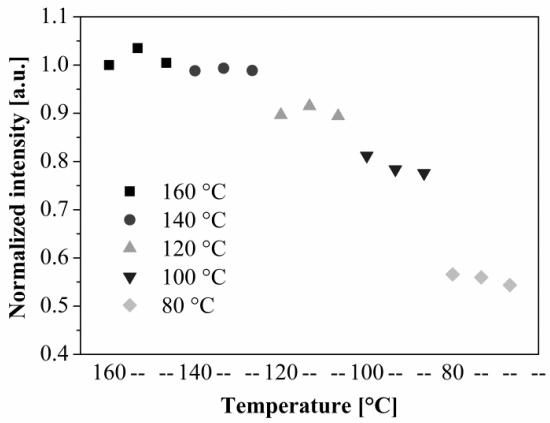

Figure 5: Normalized intensity of PE_{115} from TG-NMR experiments at different temperatures. Each temperature level was measured three times at 20 °C intervals. Time spent between two experiments at one temperature level was 30 minutes.

As seen in Figure 5 the changes in the signal intensities are solely a function of temperature variation and do not depend on the duration of the temperature step. This confirms that the system PE_{115}/ NG/ODCB-d4 was in thermodynamic equilibrium i.e., the influence of a kinetic factor can be ruled out as a key reason for the decreasing PE_{115} signal intensities (Figure 3) above the crystallization step.

To evaluate the possibility of induced crystallization in the presence of NG at elevated temperatures a poly (ethylene-*stat*-1-octene) with 37 wt. % comonomer content (E/O_{37}) was chosen. This sample was concluded to be highly amorphous for the experimental condition described in this work from separate CEF experiments. The results from the TG-NMR experiment conducted with E/O_{37} are shown in Figure 6.

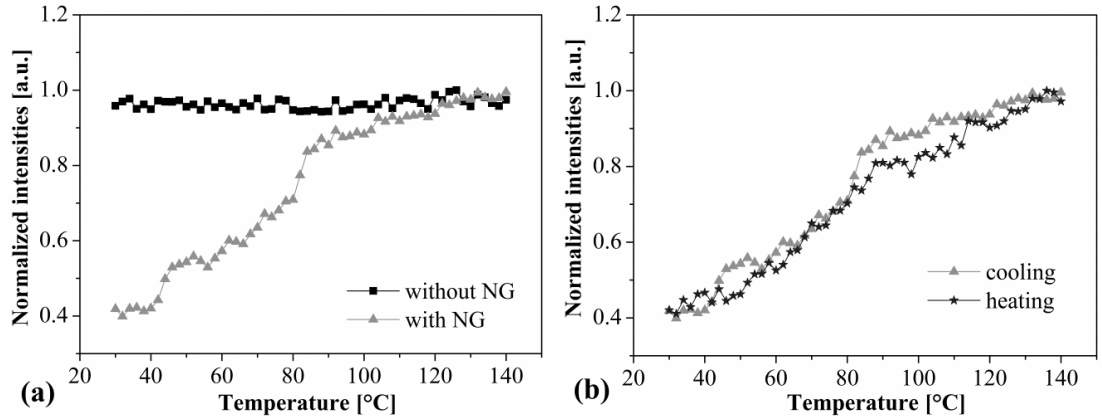

Figure 6: Normalized intensities of (E/O_{37})/PDMS in TG-NMR experiments using ODCB-d4 (a) with and without NG in temperature array 140 → 30 °C in 2 °C steps; and (b) comparison of cooling and heating process in the temperature array 140 °C → 30 → 140 °C in 2 °C steps in the presence of NG.

Without NG no crystallization related decrease in E/O_{37} signal intensity was observed, concurrent to the close to amorphous nature of the E/O_{37} sample in the cooling cycle. Whereas, in the presence of NG a decrease the signal intensities from methyl and methylene groups signal intensity of E/O_{37} was observed from ~ 130 °C, with a sharp increase at ~ 100 °C. The fact that the highly amorphous E/O_{37} is fully soluble in ODCB at 30 °C confirms that this decrease from ~ 130 °C downwards is not due to induced crystallization but from adsorption of the E/O_{37} out of the solution onto the NG surface. Figure 6 (b) shows that the decrease in E/O_{37} signal intensity is reversible without any significant hysteresis. Crystallization from solution and re-dissolution typically show a hysteresis, as can be seen from the differences in crystallization temperature from CRYSTAF and re-dissolution/elution temperature in TREF.[53] This is unlike an adsorption/desorption mechanism of PE/Graphite/ODCB which doesn't show hysteresis as chromatographic experiments have shown that the adsorption of PE on graphite[54,55] in the presence of solvent occurs at the same temperature as the elution temperature in TGIC which signifies desorption of PE from graphite[36,37] in the presence of the same solvent, e.g., ODCB. Thus the absence of a hysteresis in Figure 6 (b) is an additional, albeit indirect, proof that the decrease in signal intensity observed in TG-NMR is the result of the adsorption of PE on the NG surface. To compare with the results obtained from TG-NMR, TGIC was conducted on E/O_{37} in a similar temperature gradient with a column packed with NG using isocratic ODCB as mobile phase. Figure 7 shows the TGIC chromatogram of E/O_{37} using the NG column.

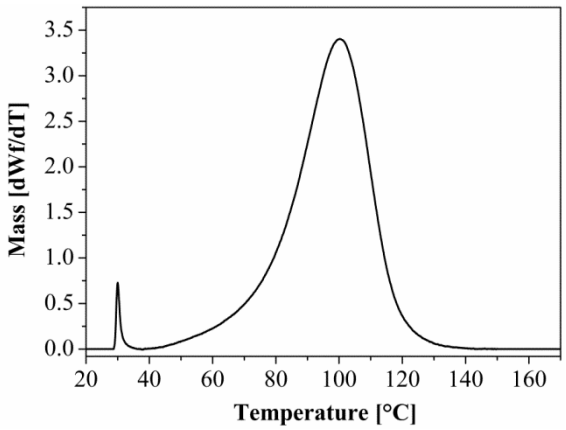

Figure 7: TGIC plot of E/O_{37} with NG as stationary phase and isocratic ODCB as mobile phase.

It can be seen that E/O_{37} elutes in the range 40 – 140 °C with the T_{pmax} at ~ 100 °C which is the region where a decrease in proton signal intensity was observed in the TG-NMR experiments (Figure 6). The small peak observed at 30 °C can be assigned to a fraction of the E/O_{37} which does not interact with the NG surface.

To further support the above conclusion, that is, the decrease in signal intensity above the crystallization temperature in solution results from interactions between the macromolecules and NG, solution DSC experiments were conducted under similar experimental conditions. In these experiments PE_{115} and E/O_{37} were dissolved in ODCB by raising the temperature up to 160 °C, and then cooled at a constant rate to 40 °C while analyzing the thermodynamic events occurring in the cooling step. The heat flow in the cooling step as a function of temperature is shown in Figure 8.

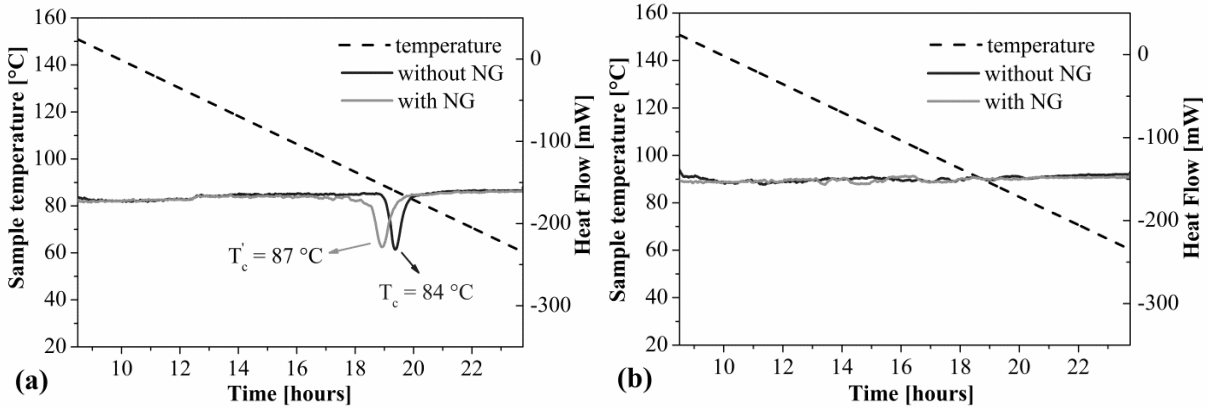

Figure 8: Heat flow as a function of temperature for Solution DSC experiments in ODCB for (a) PE_{115} and (b) E/O_{37} with and without NG.

In the presence of NG the crystallization temperature (T_C) of PE_{115} shifted higher by 3-5 °C as shown in Figure 8 (a), while no crystallization related exotherm could be observed for the amorphous E/O_{37} (Figure 8 (b)). From solution DSC at these experimental conditions the thermodynamic events related to the adsorption were not observed conclusively as adsorptive interactions are based on weak London dispersion forces.[42-47] However, induced crystallization related peaks, if present, could be observed as their resulting exothermic heat flow would be large enough to be detected. No induced crystallization related transitions were observed in Figure 8 at 150 – 100 °C for PE_{115} and from 100 °C for E/O_{37} where a decrease in proton intensities was observed in TG-NMR and peak maxima were observed in the TGIC experiment. The fact that the concentration of a E/O_{37} copolymer decreases in the presence of NG upon reducing the temperature lead to the conclusion that the mechanism of interaction between the graphite and the macromolecules is based on adsorption. This is further substantiated by the full reversibility upon heating without any hysteresis between heating and cooling cycle. Additional evidence comes from solution DSC, which shows no thermodynamic event due to induced crystallization occurring in the system PE/NG/ODCB.

CONCLUSION

Experimental parameters for Temperature Gradient ^{1}H NMR (TG-NMR) were established for the first time to quantitatively study the interaction of polyethylene homo- and copolymers with graphite in the presence of ODCB. The different interactions were investigated by monitoring the equilibrium in the polyethylene/NG/ODCB system as a function of temperature for a homopolymer PE (PE_{115}) and a highly amorphous poly (ethylene-*stat*-1-octene) containing 37 wt. % 1-octene (E/O_{37}). TG-NMR of PE_{115} showed a sharp crystallization related decrease in intensity at 100 – 80 °C both with, and without NG. In the presence of NG, another reduction in proton intensity was observed in the temperature range 150 – 100 °C which coincided with the elution temperature from the analogous TGIC experiment of the PE_{115}. This decrease in PE_{115} signals was speculated to arise from three possibilities; - unstable thermodynamic equilibrium of the system, induced crystallization in ODCB at elevated temperatures due to a nucleating effect of NG, or adsorption onto NG in the presence of ODCB. By extending the duration of the TG-NMR experiment the possibility of unstable thermodynamic equilibrium was excluded. To investigate the two remaining possibilities the TG-NMR experiment was conducted on E/O_{37}, which was confirmed to be

highly amorphous at the experimental conditions under observation. A similar decrease in signal intensity was observed from ~ 100 °C in E/O_{37} as was seen earlier for PE_{115} starting from ~ 150 °C. The lower temperature of concentration decrease for E/O_{37} was due to the presence of 1-octene branches. The observed concentration decrease was completely reversible and no thermal hysteresis was observed which gave evidence of an adsorption/desorption mechanism in polyolefin/graphite/ODCB like systems. The temperature of reduction observed for E/O_{37} from TG-NMR matched to the elution temperatures from the analogous TGIC experiments thus strongly suggesting similarity in the involved interactions. Solution DSC experiments on PE_{115} and E/O_{37} conducted under similar experimental conditions gave no hint for induced crystallization of PE_{115} and E/O_{37} from solution, thus confirming the conclusions from the TG-NMR experiments. As a consequence, it could be stated that TGIC based separations are based on adsorption without induced crystallization. The TG-NMR experiments conducted for PE_{115} also showed abnormally high signals at temperatures appreciably lower than the crystallization temperature. This high residual signal intensity was not observed in the CEF experiment conducted at similar concentrations. For the first time such signal intensities have been detected for PE macromolecules below the crystallization temperature from solution and it may be speculated that these are the result of mobility in the crystallized domains of PE_{115} in the ODCB solution at dilute concentrations. The TG-NMR method developed here provides a powerful technique for screening potential stationary phases with regard to their selectivity in interactive chromatography. The results may in the same sense be used to identify suitable experimental parameters for interactive liquid chromatography.

ACKNOWLEDGEMENT

This research is a part of the research collaboration between the Fraunhofer LBF, Darmstadt and the Dow Chemical Company, USA. The authors acknowledge the fruitful discussions with Dr. Tibor Macko from Fraunhofer LBF and Drs. Andrew Pasztor Jr. and John Lyons from the Dow Chemical Company

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Studying the interactions of polyethylene with graphite in the presence of solvent by High Temperature Thermal Gradient Interactive Chromatography, Thermal Gradient Nuclear Magnetic Resonance Spectroscopy and Solution Differential Scanning Calorimetry

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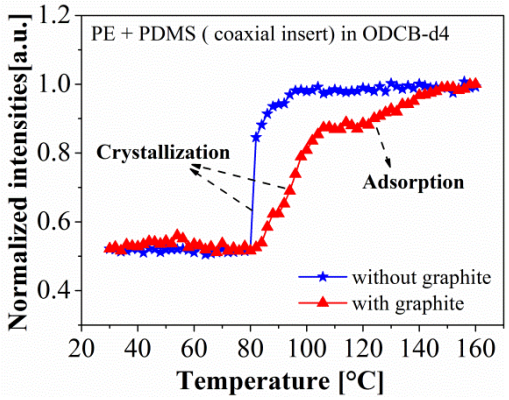

7. Summary and Conclusions

Polyolefins are, by volume, the most important synthetic polymers with an annual production expected to reach 200 million metric tons by the year 2020. Due to their widely adaptable end-use properties, paired with a good cost/performance ratio, they continue to find acceptance in novel and diverse applications. This versatility arises from the ability to control molecular heterogeneities as a result of advances in catalyst and process technology. At the same time, this creates the need to develop appropriate and more comprehensive analytical methodologies for molecular characterization. The molecular heterogeneities in polyolefins can to a large extent be defined by the molecular weight distribution (MWD) and the chemical composition distribution (CCD). Recently, high temperature high performance liquid chromatography (HT-HPLC) in the form of high temperature liquid adsorption chromatography (HT-LAC) has become an emerging tool to determine the CCD of polyolefins. The aim of the work presented in this thesis was to develop improved methodologies based on HT-LAC for the compositional separation of polyethylene (PE) and investigate the underlying mechanism of the separation. The development of HT-LAC as a tool for determining the CCD of polyolefins is the result of the discovery that porous graphitic carbon (PGC) can reversibly adsorb polyolefins and olefin copolymers from solution and hence can be applied as a stationary phase material. The research presented in this thesis is divided into five parts that have led to publications which in cumulative form encompass the

major conclusions as given below. Upon giving a concise synopsis on the state of the art the conclusions will be summarized for each part separately.

Depending on the mechanism of separation HT-HPLC techniques may be divided into high temperature size exclusion chromatography (HT-SEC) and HT-LAC. HT-SEC is routinely applied to determine the MWD of polyolefins, whereas HT-LAC has been developed recently to determine the CCD of the same. According to the variant which governs the separation HT-LAC can further be classified into solvent gradient (HT-SGIC) and thermal gradient (HT-TGIC) interactive chromatography In HT-SGIC the analyte is separated by applying a gradient from an adsorption promoting solvent to a desorption promoting one at isothermal conditions, whereas in HT-TGIC the same is achieved by applying a temperature gradient with the mobile phase being isocratic. At the boundary between HT-SEC and HT-LAC a third mode of chromatography called high temperature high temperature liquid chromatography at critical conditions (HT-LCCC) exists, which will be described for the first time as part of this thesis. The interrelationship between the distributions with regard to composition and molecular weight can be studied in a cross fractionation approach by coupling the separations with respect to the molecular parameters. Technically this has been realized in the form of two dimensional high temperature liquid chromatography (2D HT-LC), which hyphenates HT-LAC and HT-SEC to unravel the bivariate CCD x MWD.

In the first part a novel single step method was developed to separate and identify n-alkanes/oligomers in PE by using HT-SGIC. n-alkanes are a component of PE as byproduct of the catalytic synthesis, and they constitute the main ingredient of waxes, oils, and gasoline products. Hence, an accurate separation and identification of alkanes is important for the industry along the entire chain of value creation of polyolefins. By prolonging the duration of the solvent gradient, reducing the difference in solvation quality between the adsorption and desorption promoting solvent, and reducing the temperature it became possible to separate linear PE with an average molecular weight in the range of 0.74 - 2 kg/mol into the constituting alkanes. The individual alkanes were identified by spiking the analyte with alkanes of known molecular weight, and by using matrix assisted laser desorption ionization mass spectrometry as complementary technique. Thus, n-alkanes with carbon numbers ranging from 18 to 180 could be separated and identified. This method was further applied to detect n-alkanes present in an industrial high density PE (HDPE) as proof of applicability.

The developed method provides a fast single step process to separate and identify n-alkanes/oligomers in PE without any prior extraction and pre-concentration work-up.

When hyphenating two HT-HPLC techniques (e.g., 2D HT-LC, HT-LAC x HT-SEC) a significant dilution of the analyte occurs when sample is fractionated in the first dimension and then transferred to the second dimension. Consequently, the intensity of the detected signal is lowered significantly leading to poor signal-to-noise ratios. Therefore, enhancing the signal intensity could be a key step towards making 2D HT-LC a valuable technique for industrial use. As part of the experiments undertaken it was found that a PE sample could be injected and adsorbed multiple times on the PGC based stationary phase of the 1st chromatographic dimension (HT-SGIC) without starting the solvent gradient. The adsorbed sample can then be desorbed in a single step with the help of a solvent gradient. This approach was successfully applied to significantly increase the detected signal and translated to an improvement in the signal to noise ratio of the 2D HT-LC separation.

The separation in HT-SEC is governed by the change in conformational entropy of the macromolecules in the mobile phase as they enter the pores of the stationary phase, while in HT-SGIC the separation is determined by the enthalpic interactions between the macromolecules and the stationary phase in the presence of a mobile phase. HT-LCCC is an important chromatographic mode at the border between HT-SEC and HT-SGIC where the enthalpic interactions balance the entropic term. As a result, the macromolecules elute independent of the molecular weight for this specific chromatographic system. Conditions for LCCC have been reported for a variety of polymers soluble at room temperature. The knowledge of conditions for HT-SEC and HT-SGIC i.e., suitable stationary and mobile phases, is a prerequisite to realize HT-LCCC. An interesting question is, therefore, if such conditions can be realized for PE. Using well defined linear PE standards of varying and known average molecular weight, and combining adsorption promoting solvents with desorption promoting ones in an iterative approach, conditions for HT-LCCC of PE were established. The determined conditions of HT-LCCC were verified by two well established empirical methods. To demonstrate the applicability of HT-LCCC for the compositional separation ethylene/1-octene (E/O) statistical copolymers of comparable molecular weight were separated according to their average 1-octene content.

The fourth part focused on improving the resolution of the separation in HT-TGIC of E/O copolymers. Until now, 1,2-dichlorobenzene (ODCB) and 1,2,4-trichlorobenzene (TCB) have been the mobile phase of choice for HT-TGIC. The development of HT-LCCC led to a better understanding of the effect which binary solvent systems have on the chromatographic elution behavior. This generated the question if binary mobile phases could be used to enhance the resolution in HT-TGIC. This was probed for the case of E/O statistical copolymers using combinations of solvents which differ in their solvation quality and adsorption promoting behavior. The solvents that were part of this study were 1-decanol, n-decane, ODCB, TCB and diphenylether. By comparing the results from the above experiments and with help of calculations it was found that 40/60 (v/v) n-decane/TCB and 30/70 (v/v) 1-decanol/TCB, enable the highest resolution of separation for E/O copolymers by HT-TGIC. These optimized systems were also applied to separate a model blend as a proof of concept.

The above study about HT-TGIC was focused on controlling the separation of the macromolecules using PGC as stationary phase and applying a temperature gradient in an isocratic mobile phase. An important question is, therefore, the nature of the interactions between the macromolecules and the graphite surface. For n-alkanes and further low MW analytes it has been established that these interactions are based on van der Waals and London forces. However, the case is different for PE because of complexities arising out of the different molecular heterogeneities in it. Additionally, PE is semi-crystalline in nature and crystallization could also play an additional role. Hence, to study the interactions in the system PE/graphite/ODCB and to understand the mechanism of HT-TGIC based separations, nuclear magnetic resonance spectroscopy (NMR) was carried out at variable temperature (TG-NMR). A challenge which had to be overcome for this purpose was the fact, that the PGC widely used as stationary phase in HT-LAC, settled in the NMR tube due to its higher density compared to ODCB. This was solved by using nanographite (NG) which had a density comparable that of ODCB. The experimental conditions were further optimized to prevent the settling of NG on the one hand and on the other hand to achieve a good signal to noise ratio for the dissolved PE. From the TG-NMR experiments it was found that the concentration of PE homopolymer in solution starts to decrease ca. 50 °C above its crystallization temperature from the solution as the temperature in the NMR tube was gradually reduced. By carrying out repeated measurements for each temperature step it could be established that this decrease is not due to a non-equilibrium state. This decrease in concentration is fully reversible when the

temperature is increased, not showing any hysteresis. An analogous decrease in concentration in solution was also found for a fully amorphous E/O copolymer. The lack of a hysteresis and the fact that also the concentration of an amorphous copolymer in solution is decreased upon cooling pointed towards the interactions between the graphite and the polymer being adsorptive and not induced crystallization. To further confirm the absence of induced crystallization, solution DSC experiments were carried out for both sample using NG and ODCB. No evidence for an exothermic crystallization event could be retrieved from the cooling cycle, thus ruling out induced crystallization of the macromolecules from solution and indirectly confirming adsorption as mechanism underlying the separation in HT-TGIC.

The above work augments the understanding of the compositional separation of the macromolecules with the help of HT-HPLC and opens new possibilities for the compositional separation of more complex macromolecules in the future. The oligomer work further extends the application potential of HT-SGIC and this work could be further extended to the separation and identification of branched oligomers. With the help of multiple injections it was possible to attain improved SNR which could prove vital for many different 2D HT-LC separations. The newly developed HT-LCCC separations in PE could be further extended to other olefinic homo- and copolymers for achieving separations based on minute differences in microstructure. The application of mixed mobile phases in HT-TGIC improved the resolution of separation for E/O and could be further extended to other solvent and polymer systems. The TG-NMR study increased our understanding of interactions in the system PE/ graphite/solvent at different temperatures. This knowledge could be utilized to better control the separations in HT-TGIC. Additionally, the TG NMR method also provides a powerful technique for the screening of potential stationary phases with regard to their selectivity in interactive chromatography.

8. Abbreviations

2D LC	Two dimensional liquid chromatography
2D HT-LC	Two dimensional high temperature liquid chromatography
aPP	Atactic polypropylene
aTREF	Analytical temperature rising elution fractionation
CCD	Chemical composition distribution
CEF	Crystallization elution fractionation
CRYSTAF	Crystallization analysis fractionation
DC	Dynamic crystallization
DSC	Differential scanning calorimetry
EGMBE	Ethylene glycol monobutyl ether
EPDM	Ethylene propylene diene monomer
ELSD	Evaporative light scattering detector
E/P	ethylene/propylene copolymer
EPDM	Ethylene propylene diene monomer
EVA	Ethylene vinyl acetate
FTIR	Fourier transform infrared
GC	Gas chromatography
HDPE	High density polyethylene
HPLC	High performance liquid chromatography
HT-HPLC	High temperature high performance liquid chromatography

HT-LAC	High temperature liquid adsorption chromatography
HT-LCCC	High temperature liquid chromatography at critical conditions
HT-SEC	High temperature size exclusion chromatography
HT-SGIC	High temperature solvent gradient interactive chromatography
HT-TGIC	High temperature thermal gradient interactive chromatography
iPP	Isotactic polypropylene
IR	Infrared spectroscopy
LAC	Liquid adsorption chromatography
LC	Liquid chromatography
LCCC	Liquid chromatography at critical conditions
LCB	Long chain branch
LDPE	Low density polyethylene
LLDPE	Linear low density polyethylene
LS	Light scattering detector
MWD	Molecular weight distribution
MMA	Methyl methacrylate
NMR	Nuclear magnetic resonance
ODCB	1,2-dichlorobenzene
PE	Polyethylene
PGC	Porous graphitized carbon
PP	Polypropylene
PMMA	poly methyl methacrylate
PS	Polystyrene
pTREF	Preparative temperature rising elution fractionation
RI	Refractive index
SCB	Short chain branch
SEC	Size exclusion chromatography
sPP	Syndiotactic polypropylene
TCB	1,2,4-trichlorobenzene
TG-NMR	Thermal gradient nuclear magnetic resonance
TREF	Temperature rising elution fractionation
VISC	Viscometer

Symbols

ΔG	Gibbs free energy difference
ΔH	Change in interaction enthalpy
ΔS	Change in conformational entropy
Đ	Dispersity
K_d	Distribution coefficient
M_n	Number average molecular weight
M_w	Weight average molecular weight
R	Universal gas constant
T	Absolute temperature
T_c	Crystallization temperature
T_m	Equilibrium melting point of the polymer/diluent mixture
T_m^0	Melting point of the homopolymer
T_{mp}	Peak melting temperature
V_1	Molar volume of the diluent
v_1	Volume fraction of the diluent
mol. %	Mole percent
vol. %	Volume percent
wt.-%	Weight percent
χ_1	Flory Huggins thermodynamic interaction parameter

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Eidesstattliche Erklärung

Affidavit

Ich erkläre hiermit an Eides Statt, dass ich meine Dissertation selbstständig und nur mit den angegebenen Hilfsmitteln angefertigt habe.

I hereby affirm that I have prepared my dissertation independently, and only with the specified resources.

Darmstadt, 16 October 2014

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Erklärung

Declaration

Ich erkläre hiermit, noch keinen Promotionsversuch unternommen zu haben.

I hereby declare that I have made no previous attempt to get a PhD.

Darmstadt, 16 October 2014